



## Hydrogen from Solar Thermochemical Cycles



### Mobility & Fuel Production

1.

#### Thermochemical Cycles

##### ► Initial Position

Research

Results

### Initial Position

The need for fuels while the human population is growing and climate is changing requires the development of the most efficient technologies that can convert the largest available energy source – solar radiation – with the smallest impact on land and water since the need for food and water are rising even faster.

Solar thermochemical cycles are a chemical reactions that recycle the incorporated substances while splitting water into hydrogen and oxygen. The necessary high temperatures are achieved by using solar towers or dishes similar to CSP plants. The overall efficiency (solar radiation to the energy content of the hydrogen) therefore can be above 20%.

Since the technologies work most efficiently in arid regions of the world the competition with agriculture is very limited. As well the water use is very low since only the amount that is split is needed. Neither intense cooling nor irrigation is necessary.

The produced hydrogen can be used in different ways either directly as a fuel in a carbon free hydrogen energy economy, or it could be processed with carbonaceous material - ideally  $\text{CO}_2$  – to yield liquid fuels, or it could be used as a storage for solar energy to produce power via fuel cells decoupled from sunshine.



100 kW HYDROSOL II Water Splitting  
Reactor in Operation, SSPS Tower,  
Plataforma Solar de Almería, Spain



## Hydrogen from Solar Thermochemical Cycles



### Mobility & Fuel Production

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#### Thermochemical Cycles

Initial Position

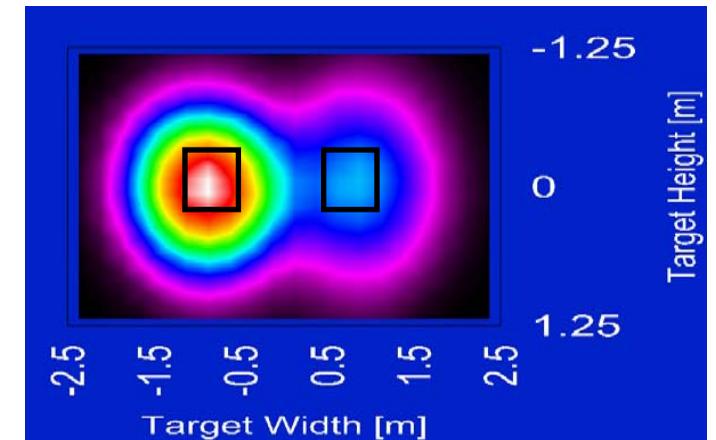
#### ► Research

Results

### Research

Several hundred thermochemical cycles are described until now. After a boom following the oil crises of the 1970s research was nearly ceased for 20 years. With the beginning of the new millennium facing rising oil prizes and climate change the technologies were reevaluated and a few were identified as most promising mainly from the metal-oxide and from the sulfur group. DLR works on both technologies in EU co-funded projects. The sulfur cycles namely the hybrid sulfuric acid cycle require temperatures up to 850°C. The main research is necessary on materials and component development, as well as on the integration with the solar concentrating system. It is most likely that this is the first technology to be demonstrated.

The metal oxide cycles need even higher temperatures above 1000°C some up to 1800°C. Therefore the main challenges are also materials and components but additionally new reactor concepts must be developed as well as efficient solar concentrators to achieve the necessary temperatures efficiently. The process models are used for evaluation and control.



Model of the solar flux distribution on the two reaction chambers of the HYDROSOL II reactor



## Hydrogen from Solar Thermochemical Cycles



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#### ► Results

### Results

Within the EU-FP6 HYDROSOL II project DLR and its partners developed and tested a fully automated 100 kW pilot reactor for the ferrite metal-oxide cycle and new ferrite materials. The reactor consists of two similar chambers each equipped with a monolithic silicon-carbide honeycomb structure on which the active ferrite is coated. While one of the chambers is heated to 1200°C to release oxygen the other chamber is run at 800°C, steam is introduced, and hydrogen produced while the ferrite keeps the oxygen. After the completion of the cycle the temperatures are switched so that a quasi continuous hydrogen flow can be realized. The work will be continued in the European Hydrogen and Fuel Cell Joint Technology Initiative.

Within the EU-FP7 HYCYCLES projects components for the sulfur cycles family are developed, like ceramic heat exchangers, separation technologies for corrosive media, and solar reactors. DLR operates successfully a new 10 kW solar reactor in the solar furnace in Cologne. It is able to evaporate sulfuric acid and split the produced SO<sub>3</sub> gas into SO<sub>2</sub> and oxygen. Besides European partners companies from the USA and research institutions from Japan and Australia take part in the project.



Assembling of the HYCYCLES 10 kW reactor for operation in DLRs solar furnace in Cologne

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DLR-Institute for Technical

Thermodynamics



## Small Traction with Fuel Cells



### Electromobility

2.

#### Small Traction with Fuel Cells

##### ► Initial Position

Research

Results

### Initial Position

Pedelecs are bicycles with an additional power source. These vehicles show a rapidly growing market attraction. If the vehicles are used as cargo bikes, the batteries need an energy back-up system, and fuel cells are the most interesting technology. Researchers at the Fraunhofer Institute for Solar Energy Systems ISE in Freiburg, together with industrial partners, develop new fuel cell powered cargo-bikes.



Cargo bike from Clean Mobile AG.

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## Small Traction with Fuel Cells



### Electromobility

2.

#### Small Traction with Fuel Cells

Initial Position

#### ► Research

Results

### Research

Investigated are Direct Methanol Fuel Cells as well as hydrogen powered Polymer Electrolyte Fuel Cells together with the related infrastructure. The fuel cells will be integrated into the Pedelecs and a demonstration project will be started to analyse efficiencies, convenience, and maintenance efforts in different applications.



Cargo bike from Masterflex-Brennstoffzellentechnik GmbH.



## Small Traction with Fuel Cells



### Electromobility

2.

#### Small Traction with Fuel Cells

Initial Position

Research

► **Results**

### Results

The demonstration project will start in mid 2010. The work programme includes the development of fuel cells, the fuel cell integration into the bikes, the installation of the fuel infrastructure for methanol and hydrogen, and the field test of different technologies in different applications.





## How to green a Vehicle Fleet?

### Integration of Electric Vehicles charged by Renewables

#### Mobility & Fuel Production

3.

#### Efficient Mobility (EffMob)

##### ► Initial Position

Research

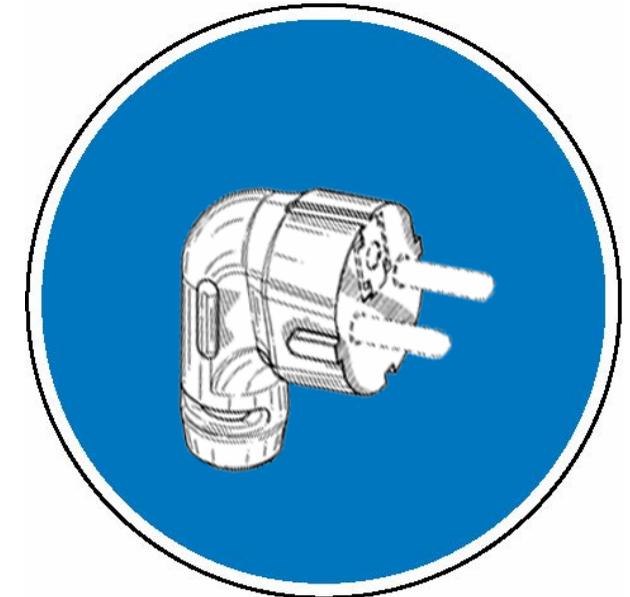
Results

### Initial Position

Badenova is a regional electric utility operator located in Freiburg/Br. The existing car fleet of approximately 500 cars runs on gasoline, diesel or natural gas. One of the project's purposes is to assess economical and ecological benefits from a future substitution of some of these vehicles by electric cars.

The project "Efficient Mobility" was initiated by the Fraunhofer Institute for Solar Energy Systems ISE, the largest solar research institute in Europe. It is financially supported by the Badenova Innovation Fond.

Within the project "Efficient Mobility", which runs through the end of 2010, Fraunhofer ISE analyses the existing hybrid vehicle fleet and tests the operation of electric vehicles as well as the use of renewable energy to power the vehicles with electricity. The target is to determine potentials of electric vehicles integration into the fleet but also into the electricity grid, to optimize the vehicle fleet based on economical and ecological criteria and to charge batteries with electricity from local Renewables (to synchronise the charging time with electricity supply from local Renewables).



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## How to green a Vehicle Fleet?

### Integration of Electric Vehicles charged by Renewables

#### Mobility & Fuel Production

3.

#### Efficient Mobility (EffMob)

Initial Position

#### ► Research

Results

### Research

First, some cars of the existing hybrid vehicle fleet will be analysed with regard to capacity utilization and primary energy use (since the engines run on different fuels). Therefore time, duration and distance data from appointments (logbook, booking system and GPS-Tracking) and energy data from cars is analysed for more than a year. Based on the results of this analysis, any supplements to the existing fleet will be simulated before an actual electric vehicle is put into use.

In order to guarantee a balanced load management, storage management and energy production management, an intelligent control is to be developed. Since the regional renewable energy production depends on solar irradiation and local wind conditions, the charging of the vehicle batteries is to be synchronized with this fluctuating electricity fed into the distribution grid. At the same time, an intelligent control provides important information about current electricity tariffs and billing.



Fraunhofer ISE – Charging Station in use with Mitsubishi i-MiEV



## How to green a Vehicle Fleet?

### Integration of Electric Vehicles charged by Renewables

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Initial Position

Research

#### ► Results

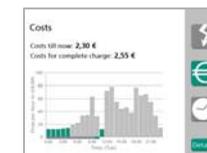
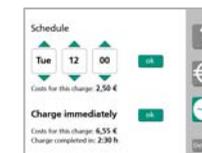
### Results

The first results of the current project are:

- distribution grid analysis for Freiburg with a large share of EVs
- Algorithms for hybrid fleet optimisation
- Link to control room (information about current energy mix)
- Prototype of a smart charging station with interface (picture)

Since the charging point is connected to the general electricity grid (as in reality) the prioritised use of Renewables will be achieved through a smart tariff system: The price for electricity (15 minutes) is calculated according to the current share of regional Renewables and grid utilisation. A large share of Renewables stands for a low price, CO2-intense energy production with smaller shares of Renewables for a high price. With this information at the charging point the user himself may decide whether to charge cheaply with 100% renewable energy (but eventually slower) or to pay more and use a smaller share of local Renewables. Hereby the availability of the vehicles, however, always has priority.

At the end, our goal is powering the electric vehicles solely with renewable energy.



Preliminary model of a smart charging station for electric vehicles to prioritise charging energy from renewable sources



## Fuelling Future Transport via Hydrogen Stations



### Mobility & Fuel Production

4.

#### Fuelling Future Transport via Hydrogen Stations

##### ► Initial Position

Research

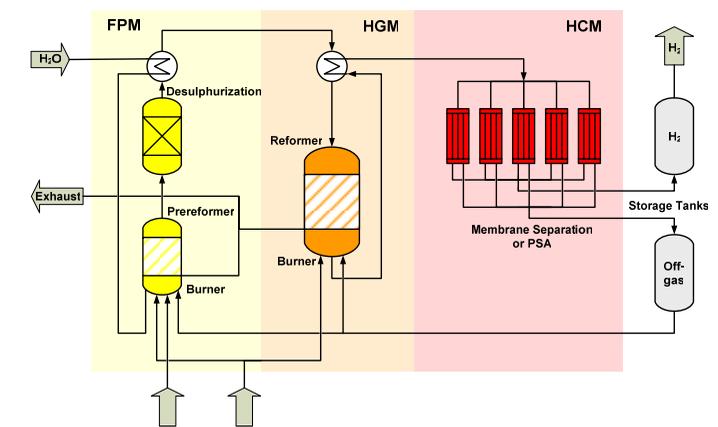
Results

### Initial Position

It is agreed on that **hydrogen** can play an important role as a **future energy carrier**. Yet there is no hydrogen infrastructure available for distribution with central production from renewables. Decentralised, small-scale units using readily available fossil or bio-fuels as feedstock are therefore needed to meet the short and midterm demand of hydrogen for transportation purposes.

The European **NEMESIS project** targeted this area under DLR's leadership. A modular approach was used to develop a multi-fuel hydrogen generation system being able to produce  $5\text{Nm}^3 \text{H}_2$  per hour from diesel and natural gas. The prototype consisted of three modules:

- Fuel Preparation Module (**FPM**): pre-reformer and desulphurization unit for liquid feedstock
- Hydrogen Generation Module (**HGM**): integrated steam reformer with off-gas burner
- Hydrogen Conditioning Module (**HCM**): PSA and membrane system for purification of the product gas to FC quality



Schematic of the **NEMESIS** process





## Fuelling Future Transport via Hydrogen Stations



### Mobility & Fuel Production

4.

#### Fuelling Future Transport via Hydrogen Stations

Initial Position

#### ► Research

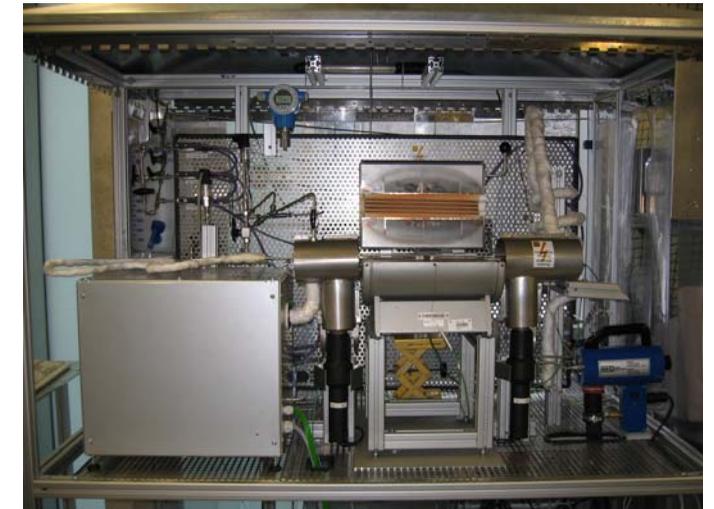
Results

### Research

The modular system approach of NEMESIS allowed for several process configurations to be pursued. DLR established a **process simulation tool** by implementation of the various components and modules into a process flowsheeting software. Energetic evaluation of the process resulted in the final concept to be realized within the prototype unit.

As liquid hydrocarbon fuels are always containing sulphur the development of **sulphur tolerant catalysts** is vital for long-term operation. In a test setup at DLR the stability of supported catalyst samples was investigated. Operating conditions of the pre-reforming step were varied and adjusted to prevent coke formation and catalyst poisoning by sulphur.

**Liquid desulphurization** by **thermal fractionation** is currently under investigation showing high potential to solve the sulphur problem upstream of the catalytic conversion step.



Catalyst testing for hydrogen production from liquid hydrocarbon feedstock at DLR



## Fuelling Future Transport via Hydrogen Stations



### Mobility & Fuel Production

4.

#### Fuelling Future Transport via Hydrogen Stations

Initial Position

Research

#### ► Results

### Results

The proof-of-principle prototype was tested for more than 200 hours producing **5Nm<sup>3</sup>/h hydrogen at 6 bars** from natural gas and diesel fuel with 8ppmw of sulphur. System start-up time was at 45 minutes and the reformer operating temperature reached 850°C. Overall **efficiency** reached **81%**.

For **implementing hydrogen in existing public fuelling stations** the use of low pressure underground storage with a two compartment tank for hydrogen and diesel in combination with a compressor and a small high pressure storage was identified as the best solution. For market introduction it is recommended to up-scale the system to 250Nm<sup>3</sup>/h hydrogen production and integrate it with other alternative fuels into one station.

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- 1 NEMESIS prototype
- 2 Insight of the Fuel Preparation Module
- 3 Hydrogen Fuelling Station



## Effects of electric cars on power generation, distribution and CO<sub>2</sub> emissions in Germany



### Mobility and Fuel Production

5.

#### Effects of electric cars

##### ► Initial Position

Research

Results

### Initial Position

IZES effected a short study on this topic by order of WWF Germany. The aim was to develop approaches evaluating a mid term evolution of power need and the effects on the power generation and distribution system as well as on CO<sub>2</sub> emissions also with regard to the legal frame conditions.

For a sound evaluation and for the classification of energy and climate policy strategies, the evaluation and the fixing of key horizon for the upcoming fields of application are crucial. Also an integrated evaluation of the technical and regulatory system is essential. With regard to the power supply system a refined analysis and evaluation concerning the power demand and the consequences for power need and load profile in the German power supply system is necessary.

<http://www.wwf.de/downloads/publikationsdatenbank/>



The car for the future?

(source: J.Matievic/WWF)



## Effects of electric cars on power generation, distribution and CO<sub>2</sub> emissions in Germany



### Mobility and Fuel Production

5.

#### Effects of electric cars

Initial Position

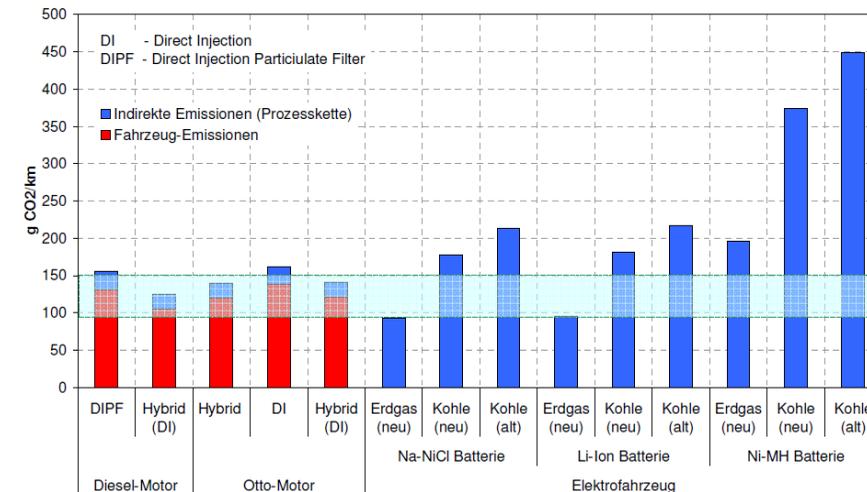
► Research

Results

### Research

In traditional drives the biggest part of greenhouse gas emissions arises directly in the motor. In grid-electrical drives these emissions come from the power plants which feed the batteries for electric cars.

As today only a few electric or hybrid cars exist, the study is focusing the key horizons until 2020 and after 2020. Until 2020 a rather small road performance for electric cars is assumed (10 billions km per year) which means that the effects on additional power generation is trivial (less than 0,5% of the total German power consumption). After 2020 and with an assumed road performance up to 240 billions km per year, the power need could increase to 4% – 10% of the total German power consumption. Also in this case it would still stay in reasonable limits. But already then a load management would be essential.



Specific emissions of different vehicle drives and process chains of energy supply as well as the emissions (light blue corridor) of a today's small electric fleet and today's mix of power plants in Germany.



## Effects of electric cars on power generation, distribution and CO<sub>2</sub> emissions in Germany



### Mobility and Fuel Production

5.

#### Effects of electric cars

Initial Position

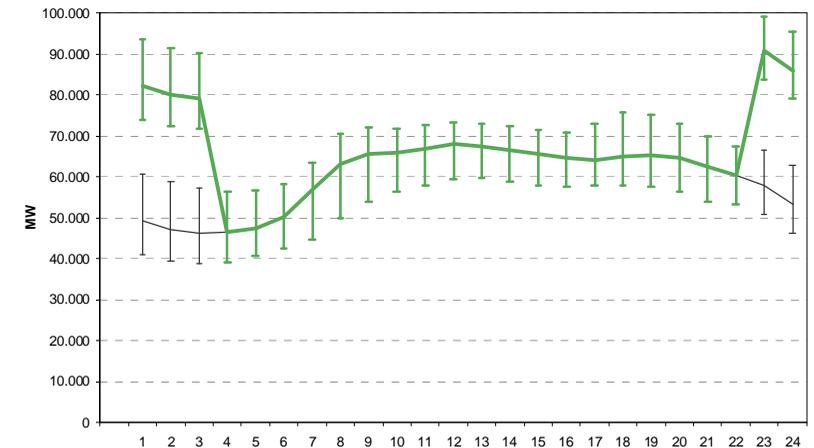
Research

► Results

### Results

1. As on European level the emission trade cap is fixed until 2020 the higher electricity will not bring higher CO<sub>2</sub> emissions. Therefore the power for electric cars has to come from a CO<sub>2</sub> free power generation based on renewable energies. This kind of vehicle drive can be a contribution to climate protection.
2. But also the contribution of electric cars to climate protection after 2020 is rather small. With an assumed driving performance of 240 billion km the CO<sub>2</sub> reduction would be at 18,2 bis 26 millions t CO<sub>2</sub> or 1,9 to 2,4% of the total German greenhouse gas emissions per year (assumption: 20 million electric cars).
3. Nevertheless an upgrading of electric cars merits political support as it makes individual traffic more climate friendly and decreases noise and concentration of noxious substances in the cities.
4. The integration of a part of the traffic system in the power system requires integrated overall evaluation methods and strategies.

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Daily load profile (mean, peak and lowest values) with a controlled recharge time of 5 hours (20 million vehicles, daily at 11pm)



## NANOSTRUCTURES FOR LIGHT-INDUCED HYDROGEN EVOLUTION

### Mobility & Fuel Production

6.

#### Solar Fuels

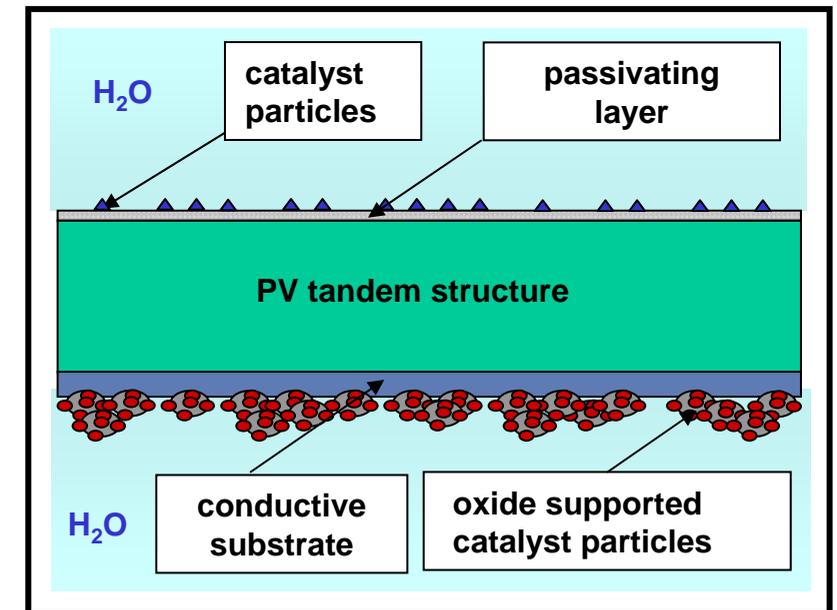
#### ► Initial Position

Research

Results

### Initial Position

The urgent need of fuel production for mobile applications from renewable energy sources is the motivation at the Helmholtz-Zentrum Berlin to develop materials, structures and devices for the generation of hydrogen from water using photocatalytic processes. Inspired by the phenomenon of water splitting occurring in photosynthesis, the project "Solar Fuels" is aimed at the preparation of corrosion-resistant photoactive semiconductor interfaces with integrated catalysts which under illumination split water into hydrogen and oxygen. The development of stable photoactive semiconductor-electrocatalyst systems and of catalytic centres and structures requires a broad materials research and an interdisciplinary approach in preparation and characterisation with respect to bulk and interface properties. The Institute Solar Fuels (in the course of formation) has recently demonstrated a surface modified InP-PV structure to generate hydrogen from sun light with high efficiency.



**Scheme of a membrane for the light-induced water splitting into hydrogen and oxygen**



## DEVELOPMENT OF A WATER SPLITTING MEMBRANE



### Mobility & Fuel Production

6.

#### Solar Fuels

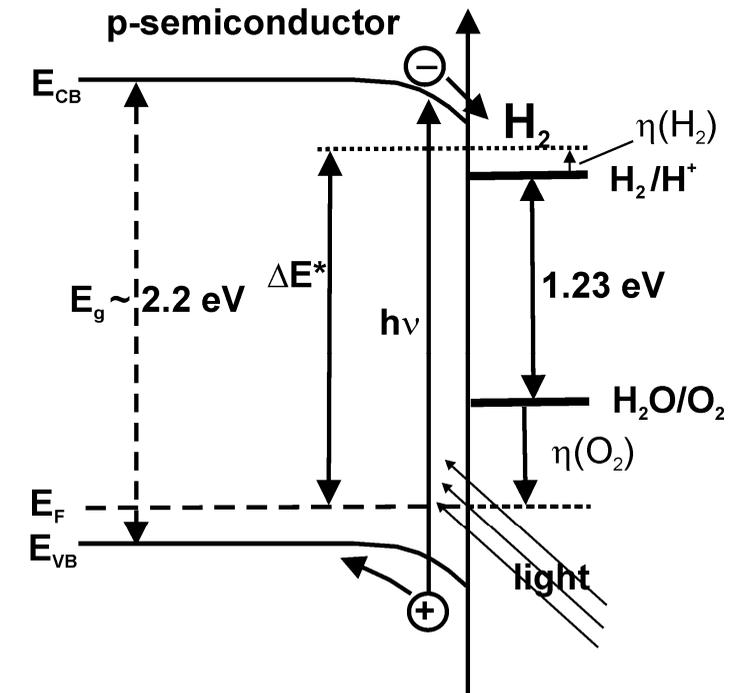
Initial Position

#### ► Research

Results

### Research topics

- Development of efficient and stable photoelectrocatalytic cells:
  - tandem heterojunction structures with attached catalysts for  $H_2$  and  $O_2$  generation
  - nanoemitter concept
- Application of combinatorial approaches and identification of promising material classes / structure families
- Demonstration of photocatalytic electrode structures



Photoelectrocatalytic half cell for the generation of hydrogen in a water splitting device



## DEMONSTRATION OF AN ELECTROCATALYTIC HALF CELL FOR LIGHT-INDUCED HYDROGEN EVOLUTION

### Mobility & Fuel Production

6.

#### Solar Fuels

Initial Position

Research

#### ► Results

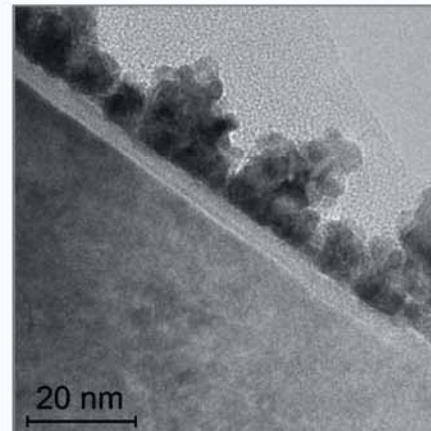
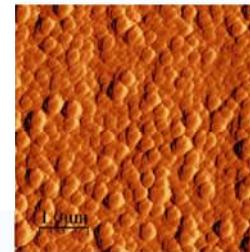
### Results

Electrochemical conditioning  
of a p-InP layer by potential  
cycling in 0.1M HCl

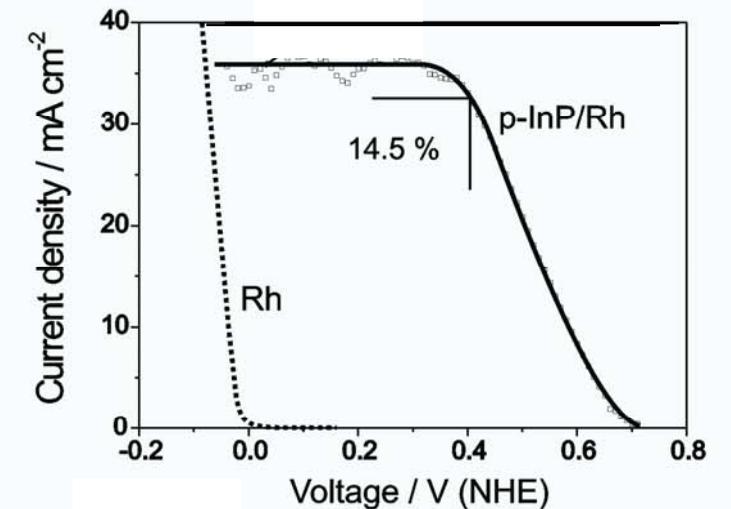
Electroplating of rhodium  
nanoparticles

Characterization of the  
electrode using

- AFM in tapping mode
- HR-TEM
- photoelectrochemistry



- AFM picture (top)
- high resolution transmission electron micrograph of a cross section of a p-InP layer (bottom)



Diode characteristic of a photoelectrocatalytic hydrogen evolving p-InP layer decorated by rhodium nanoparticles as catalyst;  
electrolyte: in a 1M HClO<sub>4</sub>  
illumination: W-I lamp of 100mWcm<sup>-2</sup>



## Hydrogen from Renewable Energy Sources



### Electromobility

#### 7. Solar Hydrogen

##### ► Initial Position

Research

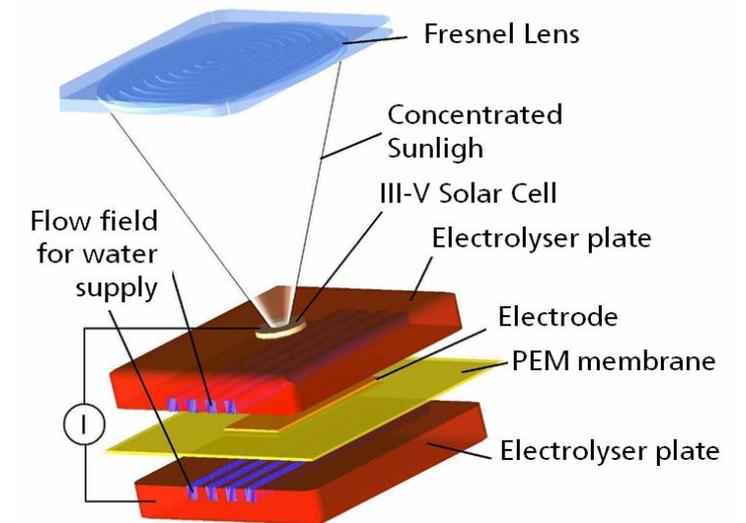
Results

### Initial Position

Hydrogen is regarded to play an important role in the future energy economy as secondary energy carrier. Based on renewable energy sources hydrogen can be produced by different approaches, e.g. fermentative conversion of organic substrates by bacteria, biological hydrogen production in photobioreactor by algae or photoelectrochemical water splitting.

The HyCon® approach is another and quite simple method to produce solar hydrogen, see figure to the right. Direct conversion from sunlight in hydrogen is achieved by the integration of a PEM electrolysis cells in a III-V multi-junction solar cell. With this patented approach highest efficiency for solar hydrogen production could be demonstrated.

*DE102004050638B3, WO2006/042650A2 and US11576939*



Production of solar hydrogen in PEM electrolysis cell directly coupled with a concentrator multi-junction solar cell.

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## Hydrogen from Renewable Energy Sources



### Electromobility

#### 7. Solar Hydrogen

Initial Position

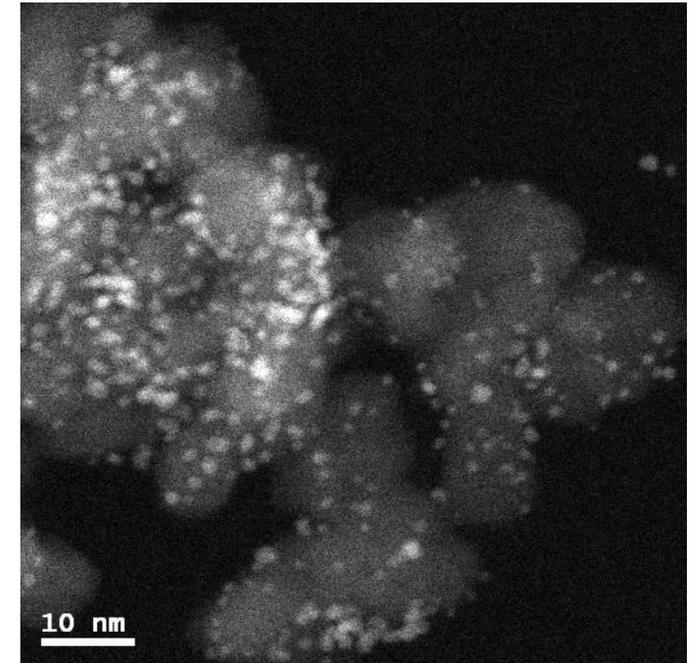
#### ► Research

Results

### Research

At first the general idea was proven with a prototype system, in which six parallel connected tandem solar cells were located under an array of six Fresnel lenses made of silicone. The concentration factor in this set-up was about 500. The six solar cells generated a photo-current of about 1 A under a typical solar illumination intensity of  $1000 \text{ W m}^{-2}$ . This current drove hydrogen production by a  $30 \text{ cm}^2$  polymer electrolyte membrane (PEM) electrolysis cell, located directly below the solar cells.

At the present main activities aim at the development of durable and low-cost electrodes development for the oxygen and hydrogen evolution reactions and a system development based on the HyCon<sup>®</sup> principle.



High resolution TEM image with uniformly dispersed Pt-Ru catalyst on Nb-doped TiO<sub>2</sub> nano-structured supports (image courtesy of University of South Carolina)



## Hydrogen from Renewable Energy Sources



### Electromobility

#### 7. Solar Hydrogen

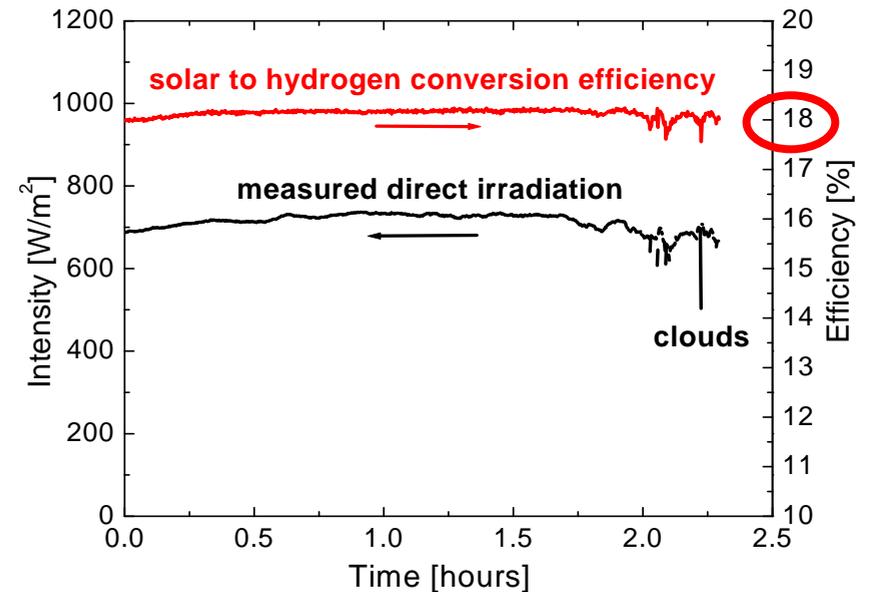
Initial Position

Research

#### ► Results

### Results

To the right outdoor test results of the first HyCon<sup>®</sup> prototype system are presented. The test set-up, consisting of six solar cells directly coupled with a PEM electrolysis cell in parallel, was mounted on a two axis tracking system in Freiburg/Germany. The thermoneutral solar to hydrogen conversion efficiency of the prototype system was measured outdoor to be 18 %. To our knowledge this is the highest solar efficiency ever reported.



Measurement of the solar efficiency to convert directly to solar energy into chemical energy of hydrogen.