Energy consumption

Energy consumption in 2020: \( \sim 20 \) TW

*Estimated Renewable Energy Resources*

- Wind energy: 2-4 TW
- Hydro-electric: 1-2 TW
- Geothermal: 12 TW (total continental)
- Biomass: 10 TW (all cultivatable land)
- Nuclear: 10 TW = 1 GW plant per 48 hrs until 2050
- Fossil + CO\(_2\) storage: Several hundred years

*Estimated Global Solar energy*

Incident on earth: **120.000 TW**

0.16% coverage gives \( \sim 20 \) TW (\( \eta = 10\%\); 816.000 km\(^2\))

*Solar irradiation on Earth in 3-day period equals all energy stored in fossil resources*
The need for storage of Solar Energy

- Intermittency of solar radiation
- Demand/supply imbalance
- Fast load changes
- Seasonal changes
Concept of artificial chemical fuels

Direct conversion

Photocatalytic: < 0.2-6 %
Solar thermal: 5-7 %

Indirect: sustainable electricity or heat
Electrochemistry: (25%)*(70-80%) = 18-20%
The principle of Solar Fuels

\[ \text{H}_2\text{O} + \text{hv} \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2 \]

- **Conduction band**
- **Valence band**
- **Band gap**
- **Hydrogen evolution catalyst**
- **Oxygen evolution catalyst**

**Semiconductor**

- **4 H\(^+\) + O\(_2\)**
- **4 h\(^+\)**
- **2H\(_2\)O**
- **2 H\(^+\)**
- **2 e\(^-\)**
Three principle device architectures

The benchmark: PV cells + electrolysis

- PV commercial, “cheap”
- Electrolysis commercial, yet costly & use noble metals

\[ \eta_{\text{overall}} = \eta_{\text{electr}} \times \eta_{\text{PV}} \approx 0.16 \]
Natural photosynthesis: how Nature does it

- Complicated multi-step system
- $\eta \approx 0.1\%$
- Reagents: water + $\text{CO}_2$
- Products: sugars (& $\text{O}_2$)
- Developed in 1~1.2 billion years

Artificial photosynthesis:

- Higher efficiencies needed (> 15% preferably)
- Simpler products compatible with energy infrastructure
  e.g., methane, methanol, hydrogen
- We need it soon!!
Photocatalysis

\[
\text{H}_2\text{O} + h\nu \rightarrow \frac{1}{2} \text{O}_2 + \text{H}_2
\]

**Crucial parameters:**

- Bandgap
- Lifetime of charge carriers
- Concentration of the defects
- Charge carriers' free path
- Stability against photocorrosion

**Requirements**

\[\eta > 10\% \quad t > 10\text{ years}\]
Physics, chemistry.....creativity needed
and device engineering......


Evolution of solar-to-fuel efficiencies

Approaches

- **CO₂ reduction**
  - Photocatalytic
  - PEC

- **H₂O splitting**
  - Photocatalytic
  - Buried PV
  - PEC
  - Metal oxide
  - Other PV
  - DSSC
  - Other PV

Solar-To-Fuel conversion efficiency (%)

- 10.00
- 1.00
- 0.10
- 0.01

Wired and monolithic devices.....

Reece et al. Science 2011, 334, 645
The real challenge: storing energy

- Preference for high energy density liquid fuels
- Need for carbon source = CO₂
Direct use of H₂

H₂ to electricity

H₂ to thermal energy

T ≈ 2200 °C (air)

P ≈ 200 bar
CO₂ capture & utilization (CCU)

Energy sources
(solar, direct or indirect)

- Well recognized target in H2020 and industry (e.g., SPIRE)
- Converting CO₂ only efficient with renewable energy

Liquid Energy Vector
Direct CO$_2$ conversion “Artificial Leaf”

"Artificial Leaf" for direct CO\textsubscript{2} utilization

Direct CO\textsubscript{2} utilization likely a dream…..

Reverse WGS: CO\textsubscript{2} + H\textsubscript{2} \rightarrow CO + H\textsubscript{2}O to syngas = CO/H\textsubscript{2}

- Waxes
- Diesel
- Olefins
- Gasoline
- Fischer-Tropsch
- Syngas
- CO+H\textsubscript{2}
- Methanol
- DME
- Ethanol
- M100, M85 DMFC

Mixed alcohols

ZnO/Cr\textsubscript{2}O\textsubscript{3}, Cu/ZnO, CuO/CoO/Al\textsubscript{2}O\textsubscript{3}

Fe, Co, Ru

Zeolites MTO, MTG

Al\textsubscript{2}O\textsubscript{3}

Cu/ZnO

Co, Rh

Co

i-C\textsubscript{4}

iso synthesis
Goals, challenges and roadmap

Stable Solar Fuels device
with 20% overall efficiency in 10 years

1. Novel light harvesting materials with high $\eta$
2. Efficient co-catalysts
3. Earth-abundant materials
4. Device integration (high-tech systems)
5. Integration into current energy infrastructure

Highly multidisciplinary efforts needed
Chemistry, Physics, Engineering
**Plasmolysis**

Benefit from the chemical reactivity of non-equilibrium plasma, considering the system energy efficiency, i.e. from CO$_2$ and H$_2$O to fuel.

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**Improve solar fuel production using plasmolysis (step)!**

H$_2$O plasma  CO$_2$ plasma / CO$_2$ plasma + H$_2$O
Plasmolysis

Benefit from the chemical reactivity of non-equilibrium plasma, considering the system energy efficiency, i.e. from CO\textsubscript{2} and H\textsubscript{2}O to fuel.

- **H\textsubscript{2}O plasma**
  - a) Plasmolysis
    - H\textsubscript{2}O → \text{plasmolysis} → O\textsubscript{2} → H\textsubscript{2}
  - b) Plasmolysis
    - CO\textsubscript{2} → \text{plasmolysis} → CO → WGS reaction

- **CO\textsubscript{2} plasma / CO\textsubscript{2} plasma + H\textsubscript{2}O**

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**Improve solar fuel production using plasmolysis (step)!**
This workshop

WORKSHOP 1 - Blauwe Zaal (Auditorium)

Solar fuels: storing solar energy in chemical bonds
Organizer dr.ir. Erik Langereis (FOM Institute DIFFER)

14h00 Introduction - The scientific challenges for solar fuels
prof.dr.ir. Richard van de Sanden (FOM Institute DIFFER)

14h20 Materials and mechanisms in solar hydrogen production
dr.ir. Jan Philipp Hofmann (TU/e)

14h35 Production of hydrogen with nanowires
prof.dr. Erik Bakkers (TU/e)

14h50 Solar fuels synthesis by efficient plasma conversion
prof. Gerard van Rooij (FOM Institute DIFFER)

15h05 Plenary discussion
Use of plasmas for CO$_2$ activation

(1) CO$_2$ = CO + O  $\Delta H = 531$ kJ/mol
(2) O + CO$_2$ = CO + O$_2$  $\Delta H = 28$ kJ/mol

Plasma excitation of CO$_2$ helps to overcome C=O bond dissociation

- High $\eta$ can be achieved under certain conditions
- CO can be used to produce fuels