Sustainable Hydrogen, a European Perspective

Prof. Dr. J. Schoonman
Delft Institute for Sustainable Energy

GCEP Hydrogen Conference

Schwab Center
Stanford University
April 14-15, 2003
• Introduction

• Sustainable Hydrogen
  o TU Delft
  o The Netherlands
  o Europe

• Concluding Remarks
World Energy Consumption 1999

- **Coal**: 40%
- **Petrol**: 23%
- **Natural gas**: 7%
- **Hydroelectric**: 7%
- **Nuclear**: 1%
- **Other (geothermal, solar, wind, wood and waste electric power)**: 22%

Estimated energy consumption: $4 \times 10^{20}$ J/year
Representative composition of fuel gases for a 300 MW (35% efficiency) coal-burning power plant.
Targets of EU RE Policy

Target RE-contribution:
• 12% in 2010 relative to 6% in 1997
• Directives for RE contributions to electricity grid

Kyoto-commitments:
• (-) 8% GHGs in 2010 relative to 1990
• Directives for RE contributions to electricity grid

EU Document: Strategy and Action Plan on RE
http://europa.eu.int/comm/energy_transport
Spirit of the Coming Age
Evolving Energy Forms

Spirit of the Coming Age
Evolving Energy Forms

- Solids
- Gases (CH$_4$ and H$_2$)
- Liquids
- Direct Electricity (hydro, nuclear, new renewables)

Share of primary energy
A Succession of Energy Technology Discontinuities

- 1800: Direct - Wood, Wind, Water, Animals
- 1850: Steam Engine - Coal 1830 - 1900
- 1900: Electric Dynamo - Coal 1900 - 1940
- 1970 - 1990: Nuclear
- 1990 - ?: CCGT - Gas
Hydrogen as an energy source

Reaction:

\[ \text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) \leftrightarrow \text{H}_2\text{O} (\text{l}) + 286 \text{ kJ/mole} \]

- Hydrogen is 3\text{rd} most abundant element
- No toxic reaction products (\text{CO}_2, \text{CO}, \text{NO}_x, \text{SO}_2, \text{etc})
- Sustainable and renewable
Hydrogen as an energy source (2)

Can hydrogen meet today’s energy demands?

Global energy demand: $4 \times 10^{20}$ J/year

H$_2$ from water: 1 GJ per 90 liters H$_2$O

Water needed: $3.6 \times 10^{13}$ liters

Oceans: $1.45 \times 10^{21}$ liters

Annual rainfall: $3.62 \times 10^{17}$ liters

There is enough water to sustain a hydrogen economy!
Hydrogen properties

How (un)safe is hydrogen?

- Not decomposing
- Not self-igniting
- Not fire-supporting
- Not toxic
- Not corrosive
- Not radioactive
- Not badly smelling
- Not contagious
- Not polluting water
- No danger to unborn children
- Not carcinogenic
Hydrogen properties (2)

- Hydrogen is lighter than air, moves rapidly upwards
- Hydrogen dilutes very fast (high diffusion coeff.)
- Tight explosion limits
- Not explosive in open air
- Social acceptance?
H$_2$ in cars

Public perception:
There’s a hydrogen bomb in my car!
Comparison with other fuels

<table>
<thead>
<tr>
<th>Fuel</th>
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- High energy content per unit mass
- Low energy content per unit volume
Hydrogen: a renewable energy carrier
Production

- Chemical hydrogen production
- Hydrogen production via classical electrolysis
- Sustainable hydrogen production from renewable energy sources: Solar and Wind energy
- Novel concepts for solar cells: the Grätzel cell and solid-state alternatives
- Hydrogen production via direct photo-electrolysis
- Biomass conversion
- Challenges
Chemical hydrogen production

The Hydrogen on Demand™ System:

NaBH$_4$ + 2 H$_2$O $\xrightarrow{\text{catalyst}}$ 4 H$_2$ + NaBO$_2$

- Solution is non-flammable
- Reaction control via (reusable) catalyst
- Controlled H$_2$ combustion
- No high pressures
- NaBO$_2$ is non-toxic
- Recycling of NaBO$_2$ into NaBH$_4$ is possible
Hydrogen production by electrolysis

Anode: $4 \text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$
Cathode: $4\text{H}_2\text{O} + 4\text{e}^- \rightarrow 2\text{H}_2 + 4\text{OH}^-$
Overall: $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$

Electrolyte composition:
Pure water ($\sigma < 5 \mu\text{S/cm}$) + 30% KOH
Hydrogen production by electrolysis

Requirements for electrolysis:
• High-purity water
• Electricity

Efficiency: 85-90%
H₂ Purity: >99.9%
H₂ production by photoelectrolysis

Photoelectrolysis: Water + Sunlight = H₂ + O₂
- Indirect photoelectrolysis
  → solar cell + electrolyzer
- Direct photoelectrolysis
  → Water splitting by photo-generated electrons

Direct PE: Holy Grail of electrochemistry!
Requirements:
- H₂/O₂ fuel value ≥ 10% of incident energy
- Long lifetime
Principle of Photoelectrolysis

Electrical wire

Sunlight

4 H₂O + 4 e⁻ → 2 H₂ + 4 OH⁻

1.23 eV

4 OH⁻ → O₂ + 2 H₂O + 4 e⁻

Overall reaction:
2 H₂O + light → 2 H₂ + O₂

Semiconductor

Water

Metal electrode
Photoelectrolysis: Previous work

Much research in 70s and 80s on sensitization by doping.

→ Insufficient control over dopants
→ Influence of dopants on optical properties?
→ Insufficient visible light absorption
Photoelectrolysis: Problems

- Stable materials that can split water show insufficient light absorption.

- Efficient light absorbers suffer from photocorrosion or have energetically unfavourable band-edge positions.

This is a materials science problem, not a fundamental limitation!
Photoelectrolysis: Opportunities

• Advances in deposition techniques
• Improved understanding of defect chemistry
• More advanced optical analysis techniques
• Improved insights into electronic structure

New opportunities for the development of efficient photoelectrodes!
Photoelectrolysis: Doped oxides

\[
4 \text{H}_2\text{O} + 4 e^- \rightarrow 2 \text{H}_2 + 4 \text{OH}^- \\
1.23 \text{eV}
\]

\[
4 \text{OH}^- \rightarrow \text{O}_2 + 2 \text{H}_2\text{O} + 4 e^- 
\]

Overall reaction:
\[
2 \text{H}_2\text{O} + \text{light} \rightarrow 2 \text{H}_2 + \text{O}_2
\]
Photoelectrolysis: Recent work

- Fractal morphologies (Everest Coatings)

- $\text{In}_{1-x}\text{Ni}_x\text{TaO}_4$, $x=0.05-0.20$ (Zou et al., Nature 414 (2001) 625)

New morphologies and materials show promising photocatalytic activities!
Photoelectrolysis: Solutions

Materials: metal oxides

• Tandem cells
  • Dye-sens. TiO₂ (red, H₂) / WO₃ (blue, O₂), 4.5% (Grätzel, Nature 414 (2001) 338)
  • p-GaAs/n-GaAs/p-GaInP₂, 12.4% (Khaselev, Science 280 (1998) 425)

• Oxides with metal 3d valence band
  • MoS₂, NiTiO₃
  • In₁₋ₓNiₓTaO₄ (?), <1% (Zou et al., Nature 414 (2001) 625)

• Sensitization by doping
  • TiO₂ doped with Cr, Fe, Mn, Cd, etc.
  • SrTiO₃ doped with e.g. Cr
Hydrogen storage

There are basically 3 different ways to store hydrogen:

• Storage in pressure tanks
• Storage as a liquid
• Storage via absorption

→ Pressure tanks: 100-350 atm
→ Liquid: $T = -253°C$
Hydrogen Storage: Energy density

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- High energy content per unit mass
- Low energy content per unit volume
Efficient storage of hydrogen is considered the biggest challenge for the development of a sustainable hydrogen economy.
Hydrogen Storage: Metal Hydrides

Examples:

• LaNi$_5$H$_6$, FeTiH$_{1.7}$
  + well-developed technology
  + room temperature operation
  - low storage capacity (< 2 wt%)

• MgH$_2$, MgNiH$_2$, (Na,Li)AlH$_4$
  + high storage capacity (> 7 wt%)
  - high temperature operation
  - relatively new technology
  - reversibility?
Hydrogen Storage: Metal Hydrides

Light-weight metal hydrides (MgH$_2$, etc):

- Operating temperature > 300°C
- Slow hydrogen uptake and release

Operating temperature can be decreased by:
- Nanocrystalline porous structure
- Transition metal oxide catalysts

Nanocrystalline composite of MgH$_2$ + 0.2% Cr$_2$O$_3$:
Desorption rate: 3 kW/kg at 250°C
→ 10 times faster than pure nanocrystalline MgH$_2$
→ 100 times faster than “bulk” MgH$_2$ powder
Hydrogen Storage: Metal Hydrides

Mechanism of catalysis is still unknown

Research opportunities:

- Optimize morphology and composition of MH composites
- Explore influence of nano-size on alloying behavior
- Structure and dynamics of H in nano-sized metal alloys and transition metal oxides
- Electronic interaction of hydrogen with metal alloys and transition metal oxides
- Defect chemistry of catalyst

Experimental work + quantum chemical modeling!
Storage for automobiles

Tank weight and volume for 6 kg hydrogen (500 km range)

- H2-gas
- liquid H2
- MgH2
- Mg2NiH4
- FeTiH2
- LaNi5H6

kg / liter

TuDelft
Delft University of Technology
Mobile applications

Automobiles

- Internal combustion
  - gasoline and hydrogen
  - high temperatures
  - fuel cell for electrical systems

- Fuel cell propulsion
  - electrical motor
  - no noise
  - very energy efficient
BMW Clean Energy 2000 Project

BMW 745h:
Motor: V8 cylinder, 4.4 l, 135 kW  Max. Speed: 215 km/h
Fuel: H₂ or gasoline  Range: 300 (+650) km
Zero noise, zero emission bus

H₂ storage

Inverter

Storage cylinders:
9 cylinders, 1548 liters, 250 bar
250 km range

Fuel cell:
4 modules, 120 kW total power
400 V output, 60°C operating temp
p=1.5 bar, H₂ consumption 8 kg/h
# TU Delft Energy Program

## Sustainable Energy: Extraction, Conversion and Use

### Electrons

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<th>Storage</th>
<th>Fundamental Aspects</th>
<th>Utilization</th>
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<td><strong>P1</strong> Goossens</td>
<td>S1 Kelder</td>
<td>F1 Warman/Siebeles</td>
<td>U1 Van der Sluis</td>
</tr>
<tr>
<td>Photovoltaic Solar Cells</td>
<td>Storage of Electricity in Li-Ion Batteries</td>
<td>Molecular Optoelectronics</td>
<td>Intelligent Power Systems</td>
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<tr>
<td><strong>P2</strong> Kearley/Picken</td>
<td>S2 Kearley/Mulder</td>
<td>F2 Mulder/de Schepper</td>
<td>U2 Van der Sluis</td>
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<td>The role of structure and dynamics in conduction in discotic supra-molecular complexes and conduction polymers for photovoltaics</td>
<td>Nanostructured Solid Electrolytes</td>
<td>Structure and Dynamics of Li-ion Anode and Cathode Materials</td>
<td>DÉNLAB</td>
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<tr>
<td><strong>P3</strong> Metselaar</td>
<td>S3 Picken</td>
<td>F3 = S6 Schmidt-Ott</td>
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<td>Thin-Film Silicon Solar Cells</td>
<td>Self-organizing LC Polymer Thin Films for Li⁺ and H3O⁺ Transport</td>
<td>Production of Well-Defined Nano-Particles and Determination of Properties relevant for Energy Storage and Conversion</td>
<td></td>
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<td><strong>P4</strong> Van Bussel</td>
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<tr>
<td>Wind Energy in the Built Environment: Characterization and Development of Conversion Principles and Integration</td>
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**TU Delft**

Delft University of Technology
ACTS

• The Dutch platform for pre-competitive research in the field of catalysis
• Cooperation of major parties from industry, academia and government

MISSION

• Initiate and support the development of new technological concepts for the sustainable production of materials and energy carriers
• Contribute to the sustainable economic growth and to the knowledge infrastructure in the Netherlands
• Attract young talent to a career in science and technology
**STAKEHOLDERS**

**CONTRIBUTIONS**
- Scientific vision
- Scientific expertise & skills in catalysis
- Education and training
- Research effort

**Academia**
- Research groups;
- Institutes;
- Scientific organisations;
- etc.

**Government**
- Ministry of Education and Science;
- Min. of Econ. Affairs;
- Min. of Environment;
- Research council;
- etc.

**Industry**
- Chemical industries;
- Commercial research institutions
- Industrial associations;
- etc.

**CONTRIBUTIONS**
- Vision on national needs
- Independent evaluation of research (quality)
- Sources of national funding
- Schemes for working with SMEs

**CONTRIBUTIONS**
- Vision on needs for economic development
- Expertise & skills in industrial catalysis research
- Integrated view & effort in development of applications
- Sources of industrial funding

**TU Delft**
Delft University of Technology
CLUSTER APPROACH

bulk chemicals
polymers & materials
detergents & textiles

ASPECT program

energy
oil refining
transport

fine chemicals
pharma
food & feed

Sustainable Hydrogen program

IBOS program
SUSTAINABLE ENERGY

POLICY

• EZ: EOS (Energy Research Strategy)
  – Secure energy supply
    (Depletion & Growing energy demand)
  – Long term developments
  – Strengths in R&D

• VROM: NMP 4 (National Environmental Policy Plan)
  – Transition to a sustainable society in 30 years
  – Transition to sustainable energy supply of prime importance
  – Solutions for the climate problems of fossil fuels
    “Global warming”
SUSTAINABLE HYDROGEN

Indeed, the transition towards renewable energy sources is necessary. For renewables to become successful, an efficient energy carrier is crucial. Comparing the options, hydrogen appears to be by far the most attractive.

HYDROGEN AS VERSATILE ENERGY CARRIER

• Clean combustion product: water
• Existing engines can be turned into hydrogen engines
• Transportation over long distances with acceptable losses
• Easy conversion into that other versatile carrier: electricity, via fuel cells
• Production from many sources: renewable and fossil, in transition period
HYDROGEN PRODUCTION

- **Biomass**
  - Gasification
  - Bio-hydrogen

- **Wind**
  - Electrolysis

- **Solar**
  - Electrolysis

- **Nuclear**
  - Electrolysis
  - Thermo-catalytic

- **Natural gas**
  - Reforming
  - Partial oxidation

- **Coal**
  - Gasification
  - In-situ gasification incl. CO₂ sequestration

- **Petroleum Coke/Residue**
  - Gasification
    - incl. CO₂ sequestration

- **Other?**
SUSTAINABLE H₂ PROGRAM

POLICY

• NWO
  - Focus on thematic programming: “Themes with Talent”
  - Excellent experience NWO-industry cooperation (Japan Program) firm basis for new consortia
  - Technology Road Map Catalysis: Energy Cluster (Long term needs of society and industry for R&D)
  - Founding of ACTS platform for fundamental-strategic research
SUSTAINABLE H$_2$ PROGRAM

BUDGET

• Total: 18 M€ for 6 years
  (excl. 18 M€ ‘in kind’ of acad. participants and ‘in house’ industrial effort)

• Funded by:
  – Ministry of Economic Affairs (EZ)
  – Ministry of Housing, Spatial Planning and Environment (VROM)
  – Dutch Research Council NWO (dpt. CW, FOM, WOTRO)
  – Commercial participants, active in the field: ECN, Gasunie, NUON, Shell, BTG
THEMES

• Hydrogen storage: materials science & hydrogen
• Implications of obtained storage options for energy systems and their management
• Integration pathways of hydrogen into energy supply allowing a gradual transition to an ultimately sustainable energy system
• Social studies concerning hydrogen as a part of the energy infrastructure
• Production options for hydrogen from fossil and renewable sources
• Separation technologies assuring “clean hydrogen”
• Hydrogen activated energy saving devices and sensors
PRESENT TECHNOLOGIES

HYDROGEN PRODUCTION
Sustainable hydrogen from fossil fuels

GOALS / OBJECTIVES
Efficient use of fossil fuels without CO₂ emissions requires
- Integration of CO₂ capture (reduce cost of capture by 75%)
- Small-scale, flexible and efficient (>85%) production of hydrogen
- Develop new re-use and conversion (sequestration) technologies

PRESENT TECHNOLOGIES
- Reforming / (Catalytic) Partial Oxidation / Autotherma using natural gas, coal and oil as fuels
- Characteristics: Efficient but large-scale and with CO₂ emissions

HYDROGEN STORAGE
New materials for high density hydrogen storage

GOALS / OBJECTIVES
- High mass density, i.e. > 6 wt%H
- High volume density, i.e. > 100 kgH₂/m³
- Easy absorption/desorption for 0<T<120 °C and a few bars
- Heat of formation around ~20 kJ/moleH

PRESENT TECHNOLOGIES
- Metal-hydrides (low wt% LaNi₅H₆: 1.4 wt%H, Mg₂NiH₄: 3.6 wt%H and relatively high heat of formation)
- Nanotubes (< 2 wt%H)
- Zeolites (< 2 wt%H)
- High pressure tanks (4 wt%H but 600 bar!)
- Liquid H₂ (1.5 wt%H loss per day!)
- Adsorption on large area materials (7 wt%H but T>300 °C)

INTEGRATION OF H₂ IN ENERGY SUPPLY
New combustion techniques using pure hydrogen

GOALS / OBJECTIVES
- Utilize combustion properties of H₂ to redesign combustion processes in energy-intensive industry
- No loss / improvement in product / process quality
- Ultra-low NOₓ emissions (< 10 ppm, air free)
- Potential for ultra-high primary efficiency

PRESENT TECHNOLOGIES
- Vast majority of energy-intensive industry uses natural gas
- High-temperature processes (T > 1400 K); dilute combustion (~20 ppm), but “conventional” heat transfer
- T < 1400 K, NOₓ > 10² ppm; conventional heat transfer
- Gas engines: ~50 ppm NOₓ at misfiring limit; new development “HCCI”. Advantages and limitations?
SUSTAINABLE H₂ PROGRAM

STATUS
• First tender completed: 6 M€ granted
• All themes covered; large initial focus on “hydrogen storage”
• First projects start in May / June 2003

PLANNED
• Appointment of researchers
• Results presented on work conferences
• Second tender in three years, focus on specific themes
  – decision by Program Committee
  – program manager ACTS: Theo Barenbrug
## TU Delft Energy Program

**Production**

- **P₁.1** Van de Krol
  - Photoelectrolysis: a Truly Sustainable Route towards Hydrogen Production

- **P₁.2** Moulijn/Mulder
  - Hydrogen Synthesis from Solar Light and Water with Hydrogel-Based Catalysts and Solid Monolithic Reactors

- **P₁.3** Ferreira/de Haan
  - Power-electronic based DC architectures for optimal Hydrogen Generation from Renewable Energy Sources

- **P₁.4 = U₁.2** Spliethoff
  - Hydrogen Production and Fuel Cells

- **P₁.5** Van Ommen
  - Hydrogen Production from Biomass using Fluidized Beds: Prevention of Agglomeration

- **P₁.6** Van der Hagen
  - Nuclear Hydrogen Production

**Storage**

- **S₂.1** Van de Krol
  - Nanostructured Metal Oxide Catalysis for Hydrogen Storage

- **S₂.2** Mäschmeyer Jansen
  - Hydrogen Storage in Zeolites

- **S₂.3** Van Veen
  - Nanostructured Light Metal Alloys for Hydrogen Storage

- **S₂.4** Hagen
  - Regenerable Fuels by H₂ Storage/Release in Liquid Bio-Organic Redox Couples

- **S₂.5** Moulijn/Mulder
  - Hydrogen Storage in Organic Molecules: the Naphthalene-Decaline Cycle

**Fundamental Aspects**

- **F₁.1** Kearley/Mulder
  - Probing of Hydrogen in Nanostructured Metal Hydride Composites

- **F₂.1** De Leeuw
  - Modelling and Simulation

- **F₂.2** Van de Krol
  - Nanostructured Metal Oxide Catalysis for Hydrogen Storage

- **F₂.3** Van der Kooi
  - Thermodynamics and Sustainable Energy

**Utilization**

- **U₁.1** Schoonman
  - Intermediate-Temperature Solid Oxide Fuel Cell: IT-SOFC

- **U₁.2 = P₁.4** Spliethoff
  - Hydrogen Production and Fuel Cells

- **U₂.1** Hagen
  - Regenerable Fuels by H₂ Storage/Release in Liquid Bio-Organic Redox Couples

- **U₂.2** Van Veen
  - Nanostructured Light Metal Alloys for Hydrogen Storage

- **U₂.3** Van der Kooi
  - Thermodynamics and Sustainable Energy

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**Sustainable Energy: Extraction, Conversion and Use**

**Protons (H₂)**

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TU Delft University of Technology
EU Policy Documents

- Strategy for the security of energy supply

- Energy for the Future

- Electricity from RE for the internal market

http://europa.eu.int/comm/energy_transport

Renewable Energy in Europe
EU Energy sources - facts

- **Coal**: cost of production in EU is 4-5 times the world price
- **Oil**: cost of production in EU is 2-7 times the world price; only 8 years’ reserve for internal use
- **Natural gas**: only 2% of the world’s reserves, some 20 years’ reserve for internal use
- **Uranium**: only 2% of the world’s reserves, some 40 years’ reserve for internal use
- **Renewables**: potential abundance, relative high costs ➔ political priority
Priorities EU energy program

- Maintaining access to conventional internal resources
- Ensuring external supplies
- Completing the internal market
- Review of energy taxation
- Major energy savings in buildings & industry
- Re-engineering the transport mix
- Directives for RE contributions to electricity grid
- Development of less polluting energy sources
- Dissemination of new technologies

Renewable Energy in Europe
Concluding Remarks

Sustainable Hydrogen

- TU Delft 2002-2007
  - Production
  - Storage
  - Characterization

- The Netherlands 2003/4
  - ACTS
    - Production
    - Storage
    - Social Acceptance
  - Ministry of Economic Affairs
    - Natural gas + H₂
      - 11000 km
      - 200 metals

- Europe - 2003/4:6 FP
  - Integrated networks
  - Centers of Excellence
  - National Activities