KUALA LUMPUR 2012 WORLD GAS CONFERENCE

25th world gas conference

"Gas: Sustaining Future Global Growth"

PRODUCTION OF 'GREEN NATURAL GAS' USING SOLID OXIDE ELECTROLYSIS CELLS (SOEC):

STATUS OF TECHNOLOGY AND COSTS

By: Mogens B. Mogensen, Department of Energy Conversion and Storage, Technical University of Denmark, Roskilde, Denmark

Date: 05 June, 2012

Venue: EF5.A: WOC5 How To Integrate Renewable Power In The NG grid

Patron: IGU International Gas Union / Union Internationale du Gaz

Host: Malaysian Gas Association

Host Sponsor: PETRONAS

Co-authors

Søren H. Jensen[1], Sune D. Ebbesen[1], Anne Hauch[1], Christopher Graves[1], Jens V. T. Høgh[1], Xiufu Sun[1], Shital Das[1], Peter V. Hendriksen[1], Jens U. Nielsen[2], Aksel H. Pedersen[3], Niels Christiansen[2], John B. Hansen[4]

[1]Department of Energy Conversion, Technical University of Denmark (DTU), Frederiksborgvej 399, DK-4000 Roskilde, Denmark.

[2]Topsoe Fuel cell A/S, Nymøllevej 66, DK-2800 Lyngby, Denmark.

[3]DONG Energy A/S, Nesa Alle 1, DK-2820 Gentofte, Denmark

[4]Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark

Introduction

- **Wish to increase the production of sustainable and CO_2 neutral energy - "green house" effect – not enough inexpensive oil**

- **Denmark aims to become independent of fossil fuel by 2050.**

  Energy strategy 2050 - from coal, oil and gas to green energy, The Danish Government, February 2011, http://www.ens.dk/Documents/Netboghandel%20-%20publikationer/2011/Energy_Strategy_2050.pdf

- **Natural to look for photosynthesis products (biomass), but not enough biomass**

  H. Wenzel, "Breaking the biomass bottleneck of the fossil free society", Version 1, September 22nd, 2010, CONCITO, http://www.concito.info/en/udgivelser.php

Enough renewable energy?

- **Fortunately, enough renewable energy is potentially available.**

- **The annual global influx from sun is ca. 3 - 4·10^{24} J - marketed energy consumption is ca. 5·10^{20} J;**

1)A. Evans et al., in: Proc. Photovoltaics 2010, H. Tanaka, K. Yamashita, Eds., p. 109.

2) Earth's energy budget, Wikipedia, http://en.wikipedia.org/wiki/Earth's_energy_budget

3) International Energy Outlook 2010, DOE/EIA-0484(2010), U.S. Energy Information Administration, http://www.eia.gov/oiaf/ieo/index.html

- **Earth's surface receives at least ca. 6 - 8,000 times more energy than we need. In deserts, intensity is higher than average at the same latitude – dry air**

Area needed

- If 0.2 % of the earth's area (ca. 1 mill. km^2 or 15 % of Australia) and if collection efficiency = 10 %, we get enough energy.

- Besides solar we also have geothermal and nuclear (fusion and fission) potential energy sources.

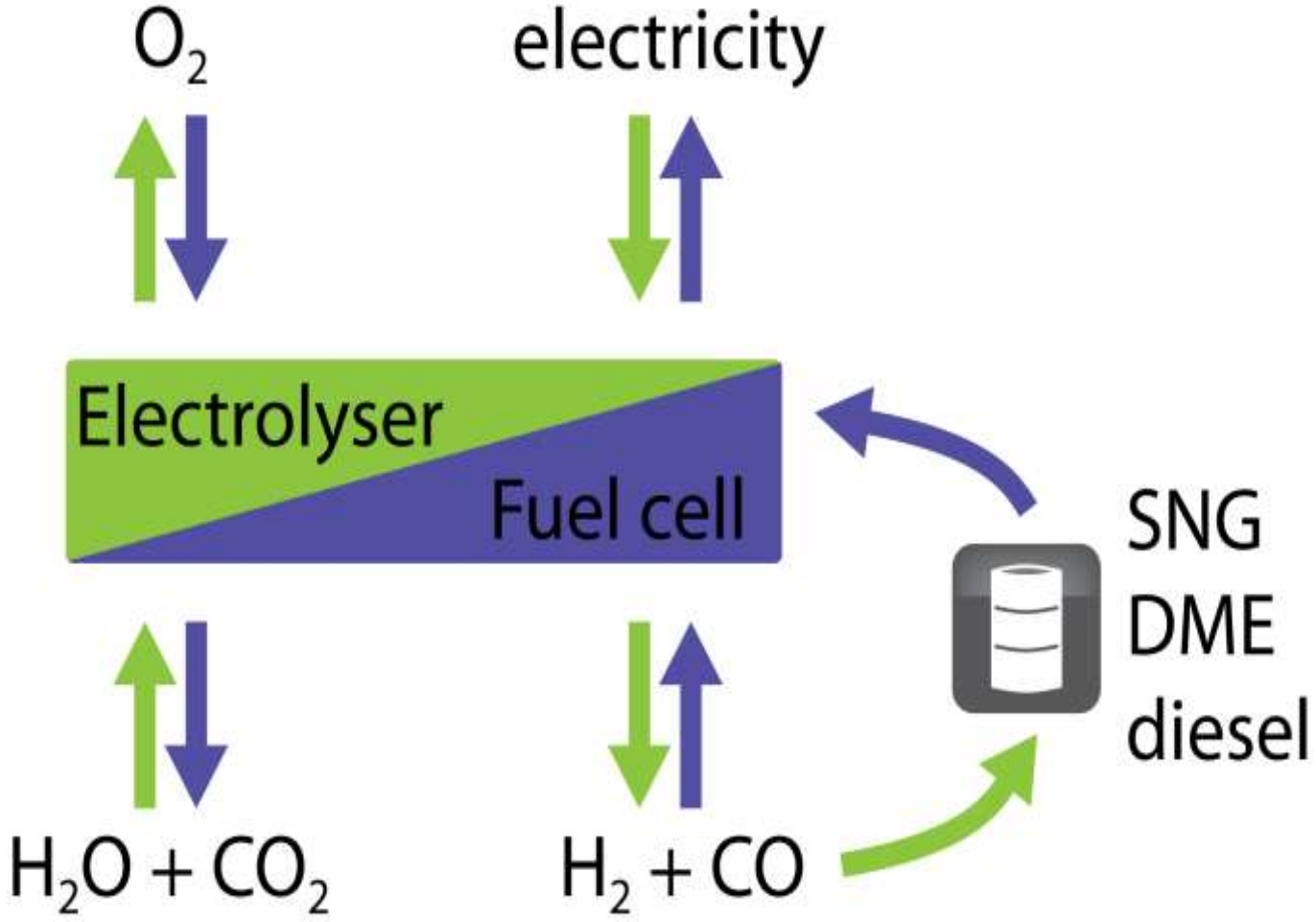
- CO_2 free nuclear - more efficient if affordable storage technology is available.

- Important part of the solar energy is actually converted to biomass, hydro and wind energy – easier to harvest.

We need electrolysis

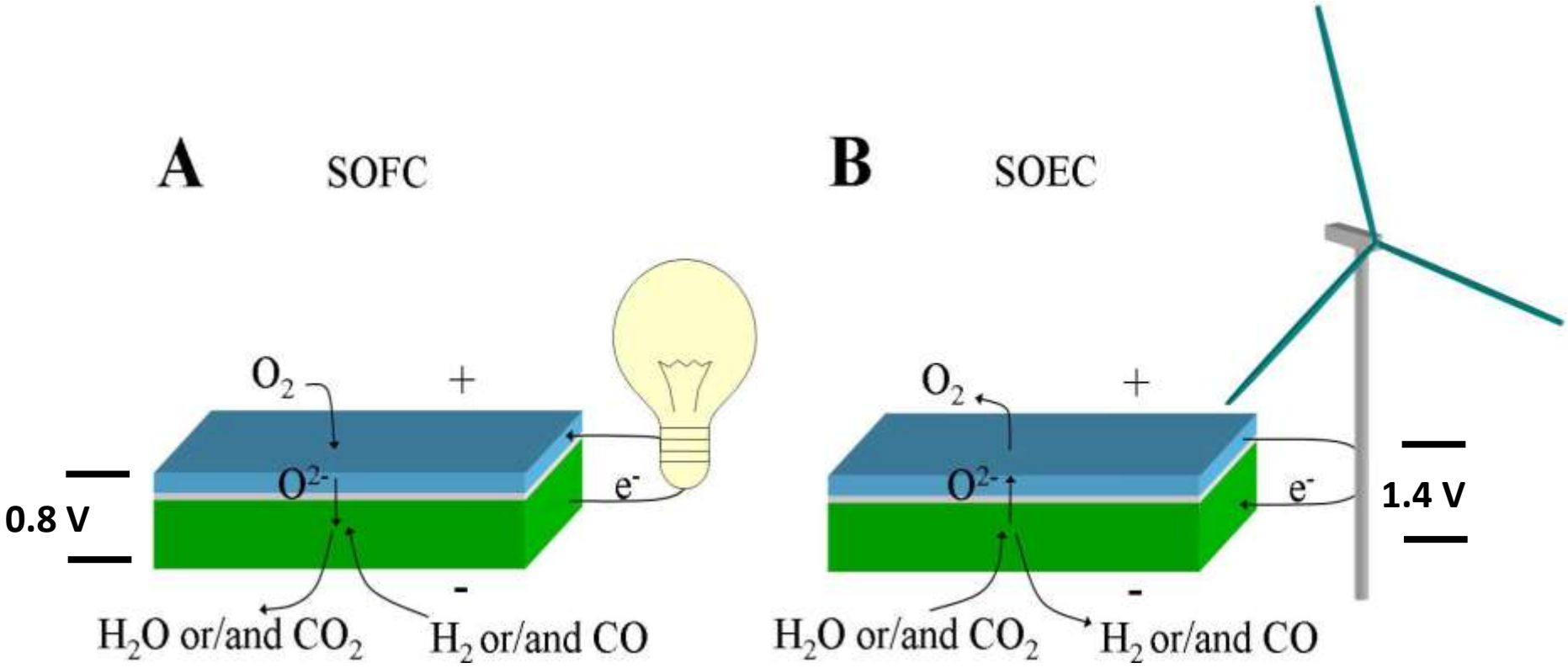
- **Many technical principles are pointed out as suitable for storage technologies:**
  - **pumping of water to high altitudes**
  - **batteries**
  - **superconductor coil (magnetic storage)**
  - **flywheels**
  - **Thermo-chemical looping**
  - **Solar Thermal Electrochemical**
  - **Photo-electrochemical HER and CO_2 reduction**
- **<u>Use electricity directly as much as possible!</u>**
- **All very important! But: first 4 are not for long distance (> 500 km) <u>transport sector</u>. 3 last are early stage research - may prove efficient in the future.**
- **Therefore, within a foreseeable future: Electrolysis is necessary in order to get enough renewable fuels!**

Reversible electrochemical cell



Reversible electrochemical cell - electrolyser for production of GNG, i.e. methane (SNG) and dimethyl ether (DME), or diesel – and fuel cell for electric power generation

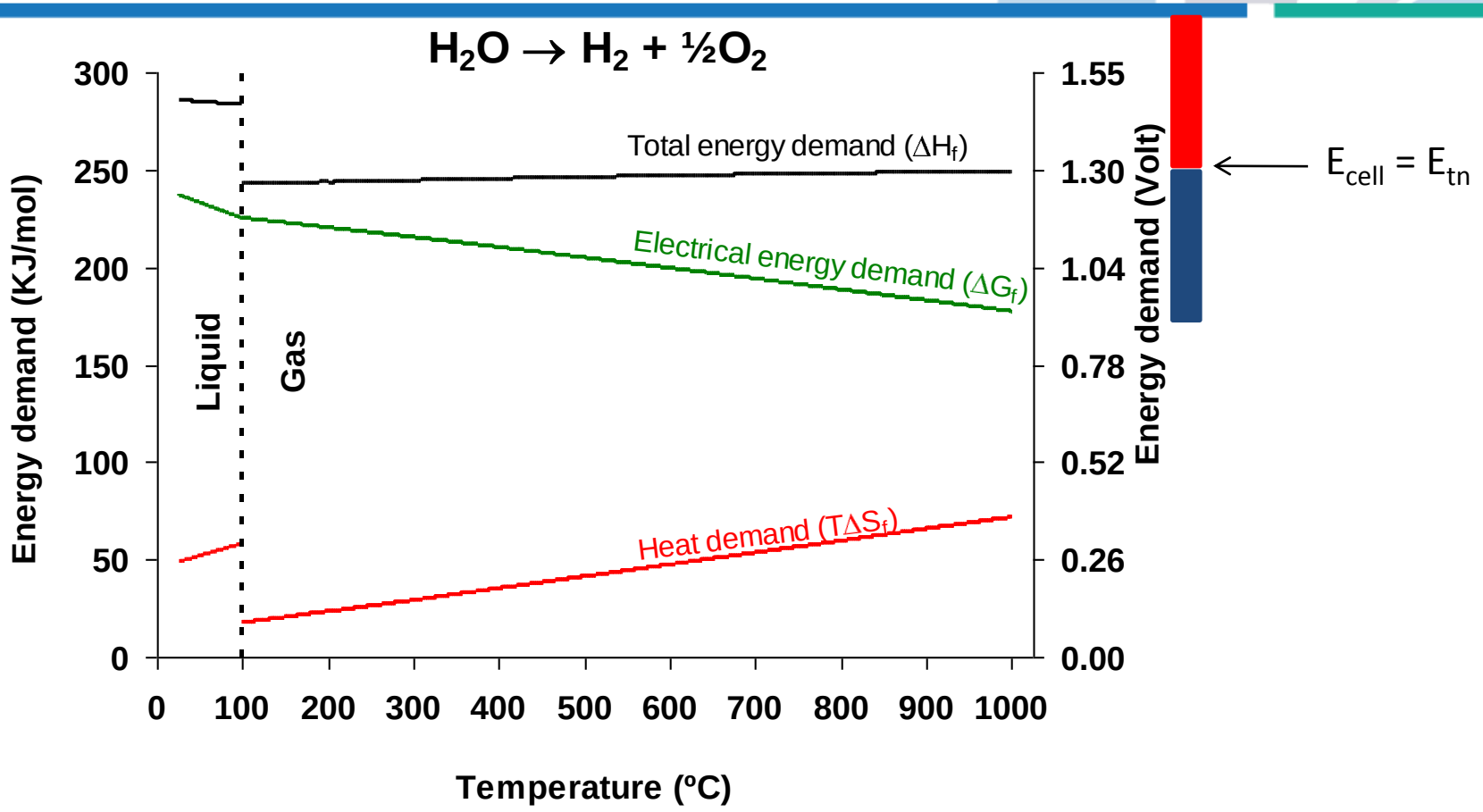
Principle of fuel cell and electrolyser (SOC)



850 °C EMF ca. 1.1 V

Working principle of a reversible Solid Oxide Cell (SOC). The cell can be operated as a fuel cell, SOFC (A), and as an electrolysis cell, SOEC (B).

Why SOC? Thermodynamics



Energy ("volt") = Energy (kJ/mol)/2F

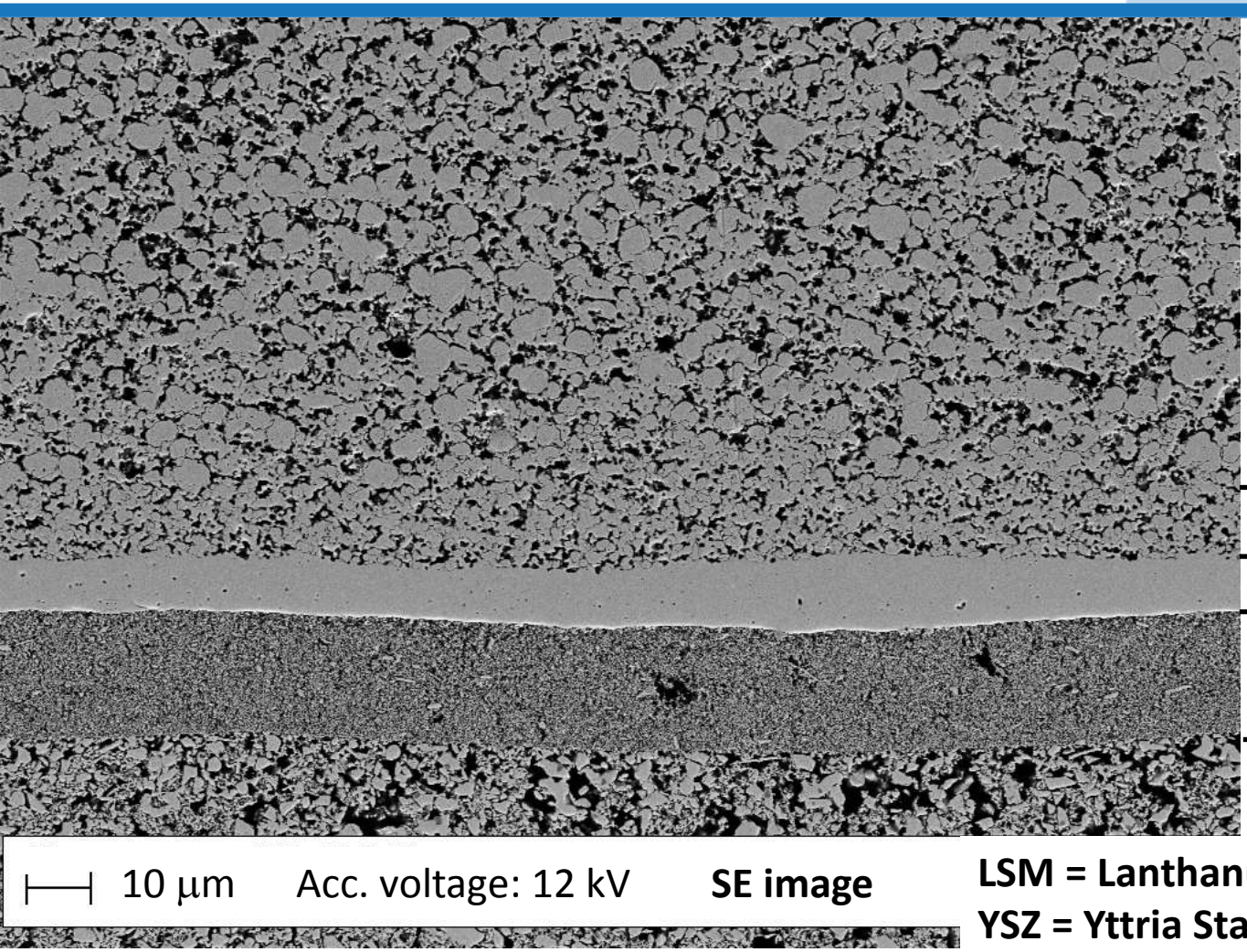
E_{tn} = $\Delta H/2F$ = Thermoneutral potential

$i \propto E_{cell} - \Delta G/2F$

Price $\propto 1/i$ [A/cm^2] ,

$\Delta H/\Delta G > 1$, $\eta = 100\ \%$ at $E = E_{tn}$ (no heat loss)

Ni-YSZ supported SOC



Ni/YSZ support

Ni/YSZ electrode

YSZ electrolyte

LSM-YSZ electrode

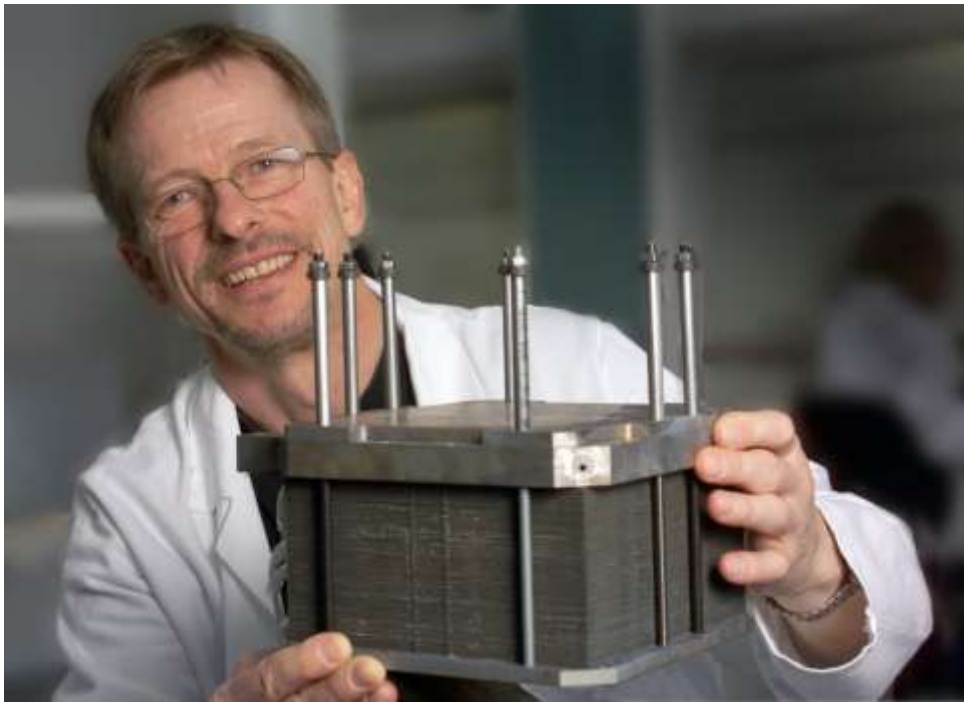
LSM = Lanthanum Strontium Manganate
YSZ = Yttria Stabilized Zirconia
Ni = Nickel

Cells stacks

- To operate at useful voltages several cells, e.g. 50, are stacked in series

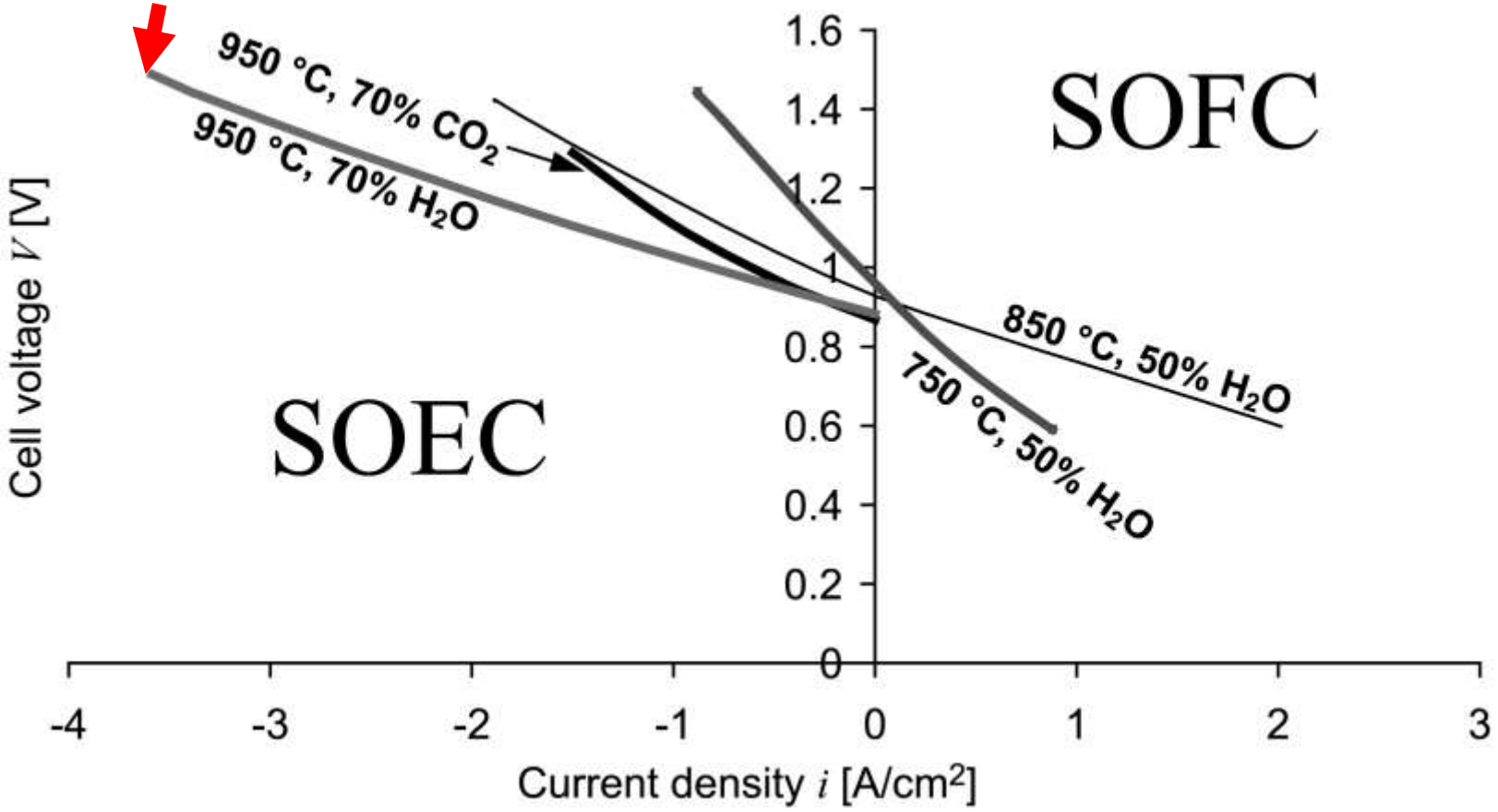
- High energy density: Stack electric power density of ~3 kW/liter demonstrated with Topsoe cell stacks in electrolysis mode

- Scalable technology:
  From kW to MW



Cell performance

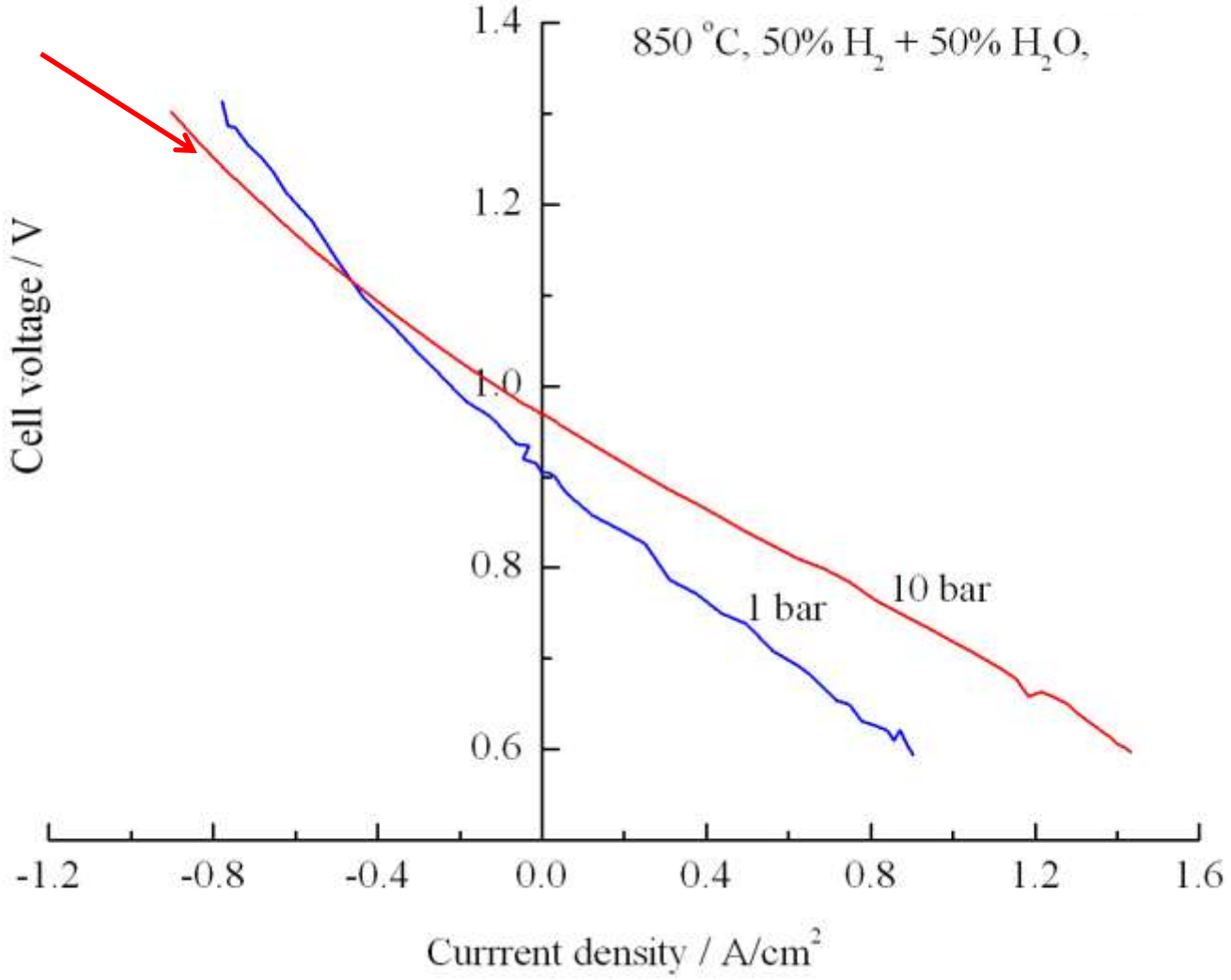
World record !



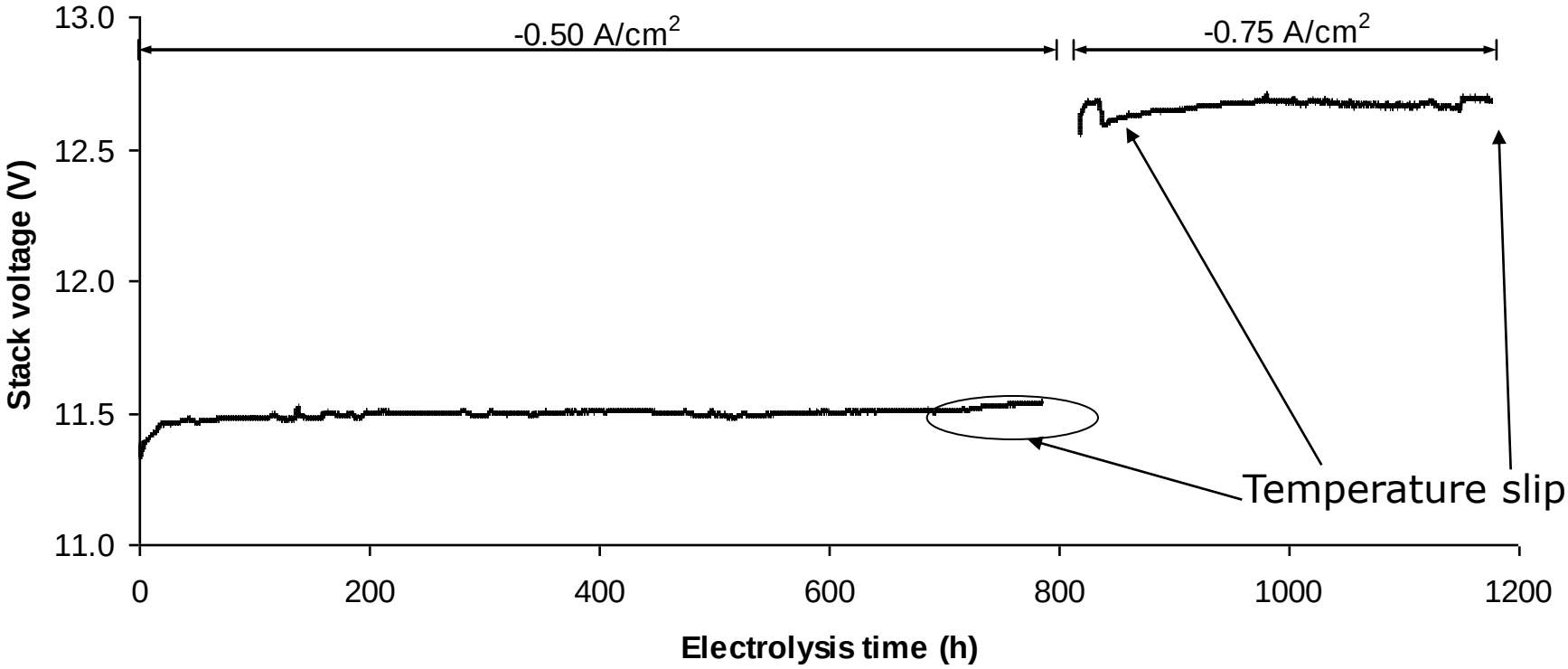
***i* - *V* curves for a Ni-YSZ-supported Ni/YSZ/LSM SOC: electrolyzer (negative cd) and fuel cell (positive cd) at different temperatures and steam or CO_2 partial pressures - balance is H_2 or CO. S.H. Jensen et al.,** International Journal of Hydrogen Energy, **32** (2007) 3253

Some early results

We get pressurized hydrogen with lower electricity input!



1 kW - 10-cell Topsoe stack – 12×12 cm², Risø DTU test



850 ºC, -0.50 A/cm² or -0.75 A/cm², 45 % CO^2 / 45% H_2O / 10 % H_2, cleaned gases.

S. Ebbesen et al., Int. J. Hydrogen Energy, **36**, (2011) 7363

Production of syngas (SOEC case)

Reaction Schemes:

The overall reaction for the electrolysis of steam plus CO_2 is:

$$H_2O + CO_2 + \text{heat} + \text{electricity} \rightarrow H_2 + CO + O_2 \qquad (1)$$

This is composed of three partial reactions. At the negative electrode:

$$H_2O + 2e^- \rightarrow H_2 + O^{2-} \qquad (2)$$

$$CO_2 + 2e^- \rightarrow CO + O^{2-} \qquad (3)$$

and at the positive electrode:

$$2\,O^{2-} \rightarrow O_2 + 4e^- \qquad (4)$$

Methane, Methanol and DME synthesis

- $CO + 3\ H_2 \leftrightarrows CH_4 + H_2O$
- Ni - based catalysts
- 190 °C – 450 °C
- 3 MPa, i.e. pressurized
- in principle possible to produce inside SOEC stack on Ni-electrode - but very low equilibrium CH_4 concentration at 650 °C and above

- $CO + 2\ H_2 \leftrightarrows CH_3OH$
- $2\ CO + 4\ H_2 \leftrightarrows (CH_3)_2O + H_2O$
- $Cu/ZnO\text{-}Al_2O_3$ catalyst
- 200 °C - 300 °C
- 4.5 - 6 MPa, again the electrolyser should be pressurized

- Another route to CO/syngas via shift reaction: $H_2 + CO_2 \leftrightarrows H_2O + CO$

Why synthetic hydrocarbons? The energy density argument

Comparison of Energy Storage Types. Only the batteries are including containers.

Storage type	MJ/L	MJ/kg	Boiling point, °C
Gasoline	33	46	40 – 200
Dimethyl ether - DME	22	30	- 25
Liquid methane	24	56	-162
Liquid hydrogen	10	141	-253
Compressed air – 20 MPa	0.1	0.4	
Water at 100 m elevation	10^{-3}	10^{-3}	
Lead acid batteries	0.4	0.15	
Li-ion batteries	1	0.5	

Why synthetic fuel? The power density argument

- **Gasoline filling rate of 20 L/min equivalents 11 MW of power and means it takes 2½ min to get 50 l = 1650 MJ on board**

- **For comparison: Li-batteries usually requires 8 h to get recharged. For a 300 kg battery package (0.5 MJ/kg) this means a power of ca. 3.5 kW i.e. it takes 8 h to get 150 MJ on board.**

- **The ratio between their driving ranges is only ca. 5, because the battery-electric-engine has an efficiency of ca. 70 % - the gasoline engine has ca. 25 %.**

Visions for synfuels from electrolysis of steam and carbon dioxide

1. **Big off-shore wind turbine parks coupled to a large SOEC – produce CH_4 (synthetic natural gas, SNG) - feed into existing natural gas net-work (in Denmark).**

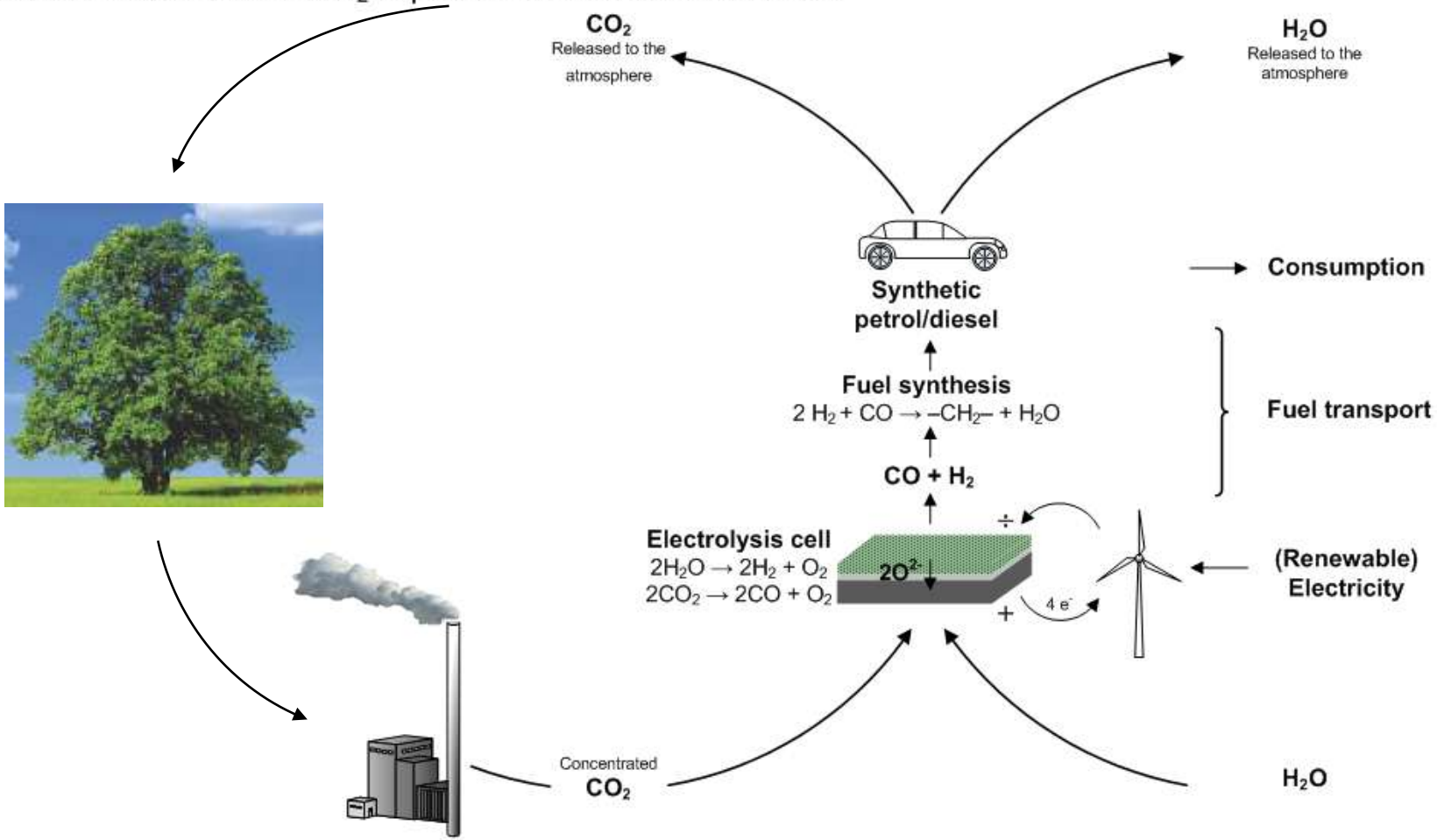
2. **Large SOEC systems - produce DME, gasoline and diesel - Island, Canada, Greenland, Argentina, Australia … geothermal, hydro, solar and wind.**

3. **Target market: replacement of natural gas and liquid fuels for transportation**

4. **All the infrastructure exists!!**

Vision, Biomass - CO_2 recycling

Short term realisation - CO_2 capture from industrial sources



New SOC production facility Topsoe Fuel Cell A/S

DTU Energy Conversion, Haldor Topsoe A/S and Topsoe Fuel Cell A/S have close cooperation around solid oxide cell technology.

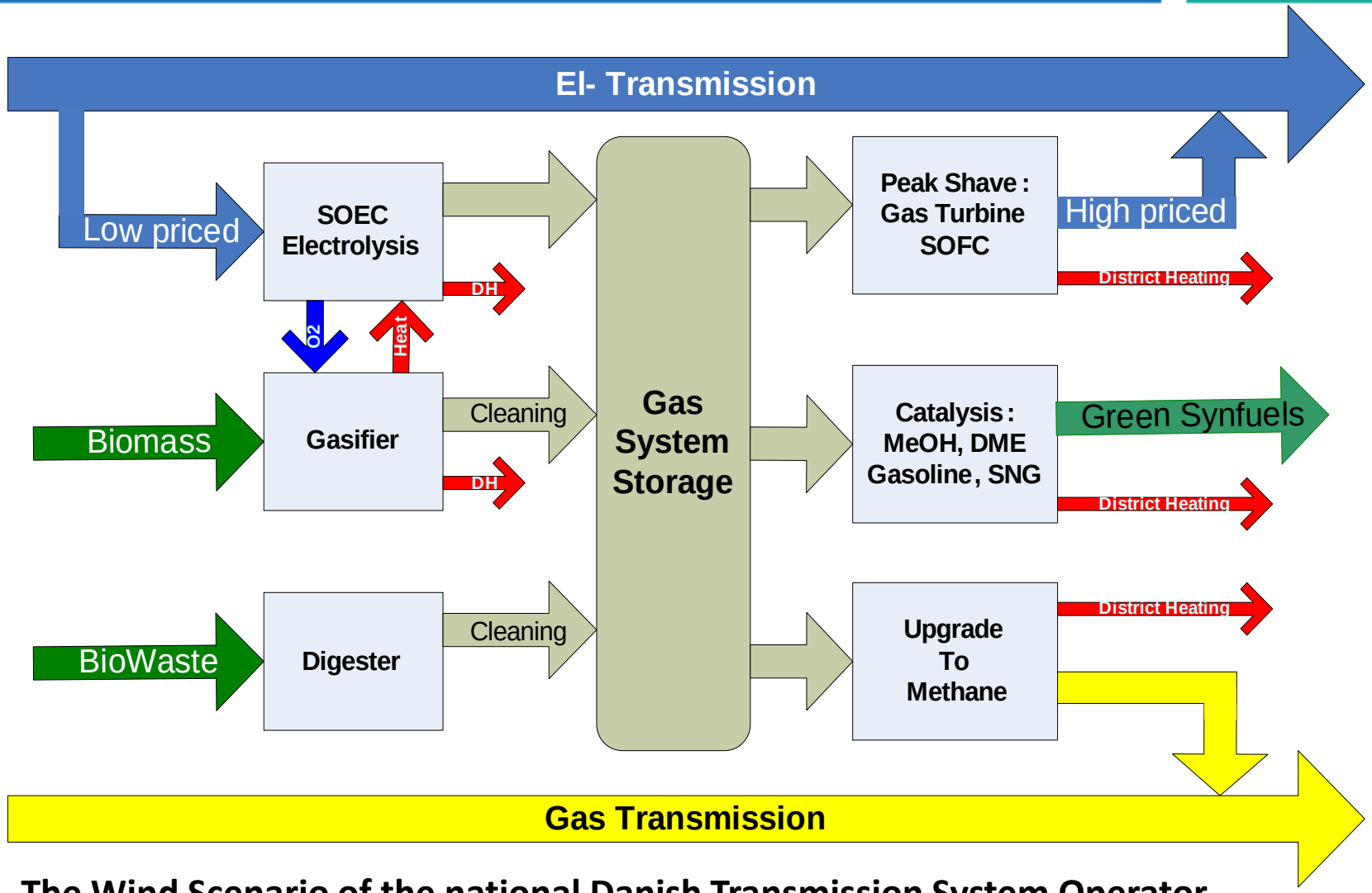
- Inauguration: April 2009
- Capacity ≈ 5 MW/yr
- Investment: >13 mio. EUR

Advanced technology – industrial relevance – low production cost

Topsoe SynGas Technologies

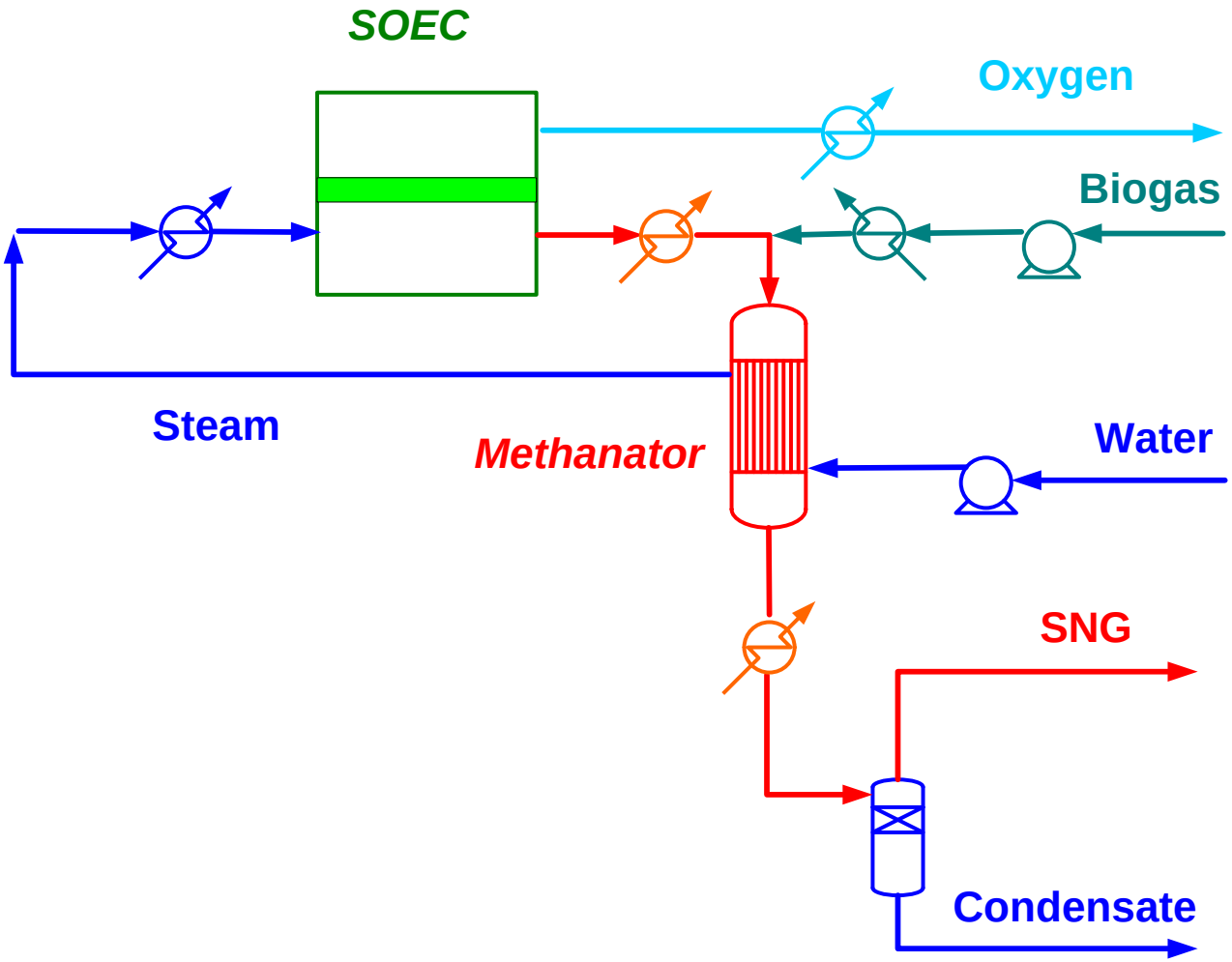
- Synthesis Gas
- Ammonia
- Hydrogen
- Carbon Monoxide
- SNG
- Methanol
- DME
- Gasoline - TIGAS

Combining Technologies

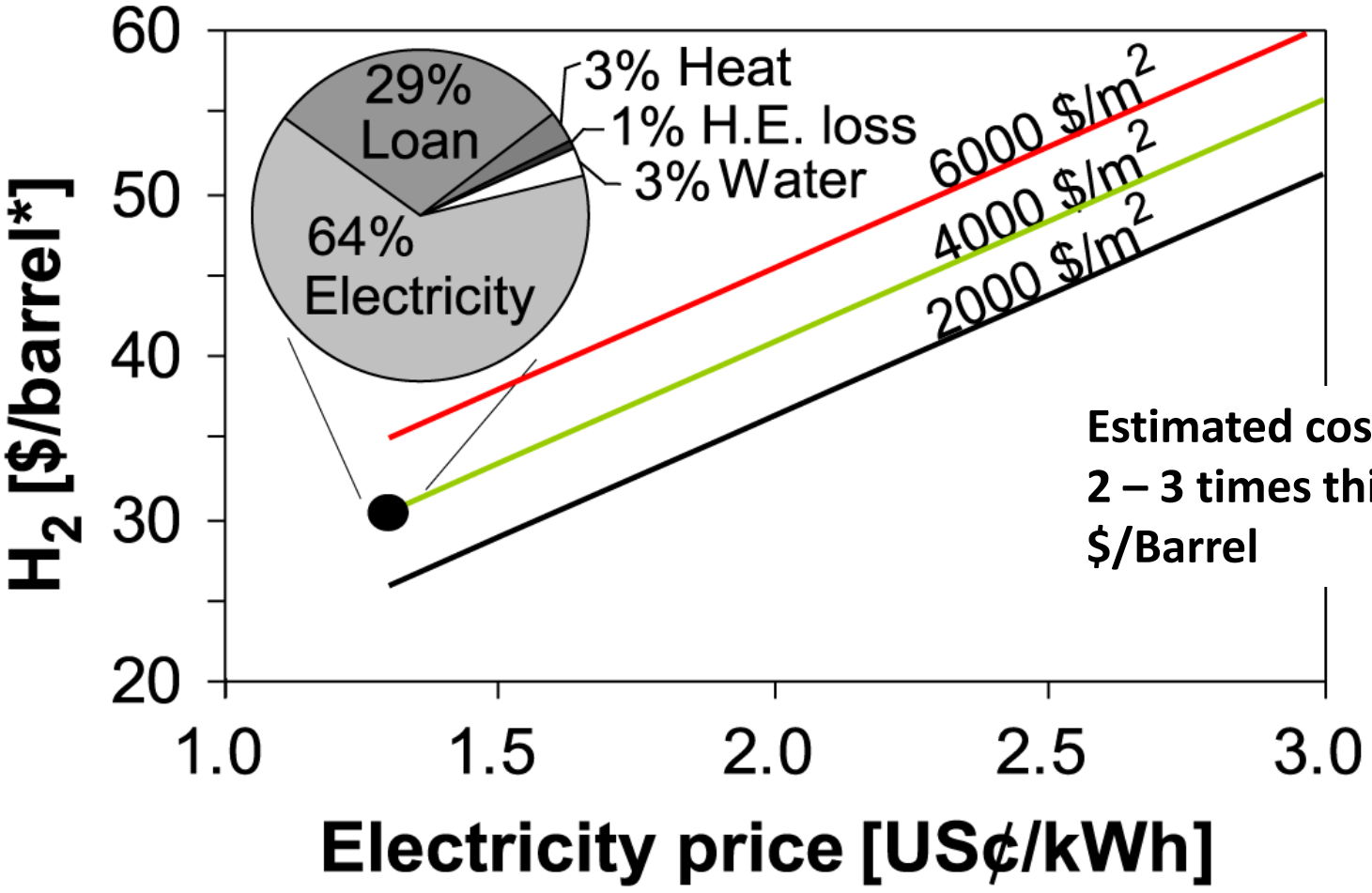


The Wind Scenario of the national Danish Transmission System Operator, Energinet.dk's visions for a fossil fuel free Denmark in 2050

Biogas to SNG via SOEC and methanation of the CO_2 in the biogas



H_2 production – economy estimation



Estimated cost of CH_4: 2 – 3 times this, i.e. 150 $/Barrel

* **Conversion of H_2 to equivalent crude oil price is on a pure energy content (J/kg) basis**

Problems in commercialization

- **Costs, costs and costs, which have different disguises:**

- **Fabrication cost**
- **Performance/efficiency**
- **Durability**

- **Risk = reliability**

- **Annoyance and disturbance of people (noise, vibration, ugly appearance,.....)**

We have to improve it all – and it is a never ending process

Acknowledgement

I acknowledge support from our sponsors

- Danish Energy Authority
- Energinet.dk
- EU
- Topsoe Fuel Cell A/S
- Danish Programme Committee for Energy and Environment
- Danish Programme Committee for Nano Science and Technology, Biotechnology and IT
- The work of <u>many</u> colleagues over the years