Perspectives of synthetic gas production from CO$_2$ and H$_2$O by high-temperature co-electrolysis using renewable or nuclear energy

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Outline

• Introduction to solid oxide cells (SOCs) - principle
• Motivations and Visions
• Brief (Danish) SOC technology status
• Economic estimates
• Concluding remarks
A solid oxide cell is an electrochemical cell, which can:

1. Convert $\text{H}_2\text{O} + \text{CO}_2$ and **electric energy** into $\text{O}_2$ (at the + pole) and $\text{H}_2 + \text{CO}$ (syngas) at the - pole, which in turn may be reformed catalytically into hydrocarbons like $\text{CH}_4$ or petrol (Fischer-Tropsch), i.e. electrolysis mode - SOEC

2. Convert $\text{O}_2$ (from air) and **energy rich gases** (e.g. hydrocarbons or ammonia) into **electric energy**. It can produce electric power in fuel cell mode - SOFC

A solid oxide electrochemical cell consists of a dense electrolyte, which is a good ion conductor and an electronic insulator. A porous electron conducting electrode is deposited on each side of the electrolyte.
Risø Ni-YSZ-supported cell (2G)

Cathode current collector, LSM, ~50µm

Electrochemically active cathode layer, LSM/YSZ, ~20µm

Electrolyte, YSZ, ~10µm

Electrochemically active anode layer, Ni/YSZ, ~15µm

Anode current collector (support), Ni/YSZ, ~300µm

LSM = (La$_{0.75}$Sr$_{0.25}$)$_{0.95}$MnO$_3$

YSZ = Zr$_{0.84}$Y$_{0.16}$O$_{1.92}$
Ni-YSZ supported cell

Ni/YSZ support

Ni/YSZ electrode

YSZ electrolyte

LSM-YSZ electrode

10 µm  Acc. voltage: 12 kV  SE image

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Risø DTU solid oxide cell

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

**Principle of SOC**

850 °C  EMF ca. 1.1 V

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

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SOFC stack and SOEC stack is analogue

A single cell gives only ca. 0.8 V.
Stacking necessary.
Stack materials

- Interconnect is usually ferritic stainless steel, ca, 22 % Cr with a number of small additives. Several commercial (or semi-commercial) steels are available.

- Gas sealing between cells and interconnect is most often a suitable SiO$_2$ based glass
Why Solid Oxide Fuel Cells (SOFC)

- High efficiency
- Fuel flexibility (natural gas, hydrogen, ammonia, ethanol, biofuels, diesel) - Internal reforming
- Low emissions
- Consists of thin layers of inexpensive ceramics (and possibly metal - Ni in the hydrogen electrode and porous metal supports).

This has been the reason for the enormous international R&D effort which has resulted in an increased performance - from ASR = 0.5 $\Omega \text{cm}^2$ at 1000 °C to 0.3 $\Omega \text{cm}^2$ at 650 °C. Note ASR follows the Arrhenius expression, i.e. exponential in temperature.
Why Solid Oxide Electrolysis Cells (SOEC)

- Electrolysis - a heat consuming process. The Joule heat contributes to the splitting of $\text{H}_2\text{O}$ and $\text{CO}_2$ molecules into $\text{H}_2$, $\text{CO}$ and $\text{O}_2$. The higher the steam inlet temperature, the less electrical energy is needed for the splitting. Self cooling.

- If high temperature heat supplied: above 100 % el. eff. (HHV)

- Synthetic fuels from $\text{H}_2 + \text{CO}$ (synthesis gas)

- The rate of the electrochemical processes is much faster at high temperature. More $\text{m}^3 \text{H}_2 + \text{CO}$ per $\text{m}^2$ cell per minute gives a better economy.

- The SOEC consists of relatively inexpensive materials and may be produced using low cost processes.

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Why synthetic fuel? I

<table>
<thead>
<tr>
<th>Type</th>
<th>MJ/l</th>
<th>MJ/kg</th>
<th>Boiling point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>33</td>
<td>47</td>
<td>40 - 200</td>
</tr>
<tr>
<td>Dimethyl ether - DME</td>
<td>22</td>
<td>30</td>
<td>- 25</td>
</tr>
<tr>
<td>Liquid hydrogen</td>
<td>(10)</td>
<td>(141)</td>
<td>-253</td>
</tr>
<tr>
<td>Water at 100 m elevation</td>
<td>10^{-3}</td>
<td>10^{-3}</td>
<td></td>
</tr>
<tr>
<td>Lead acid batteries</td>
<td>0.4</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>Li-ion batteries</td>
<td>1</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>
Why synthetic fuel? II

• 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 %.
Thermodynamics

$\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$

Energy demand (KJ/mol)

Energy demand (Volt)

Temperature (°C)

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

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CO₂ → CO + \( \frac{1}{2} \)O₂

Total energy demand (\( \Delta H_f \))

Energy demand (KJ/mol) vs. Temperature (°C)

Energy demand (Volt) vs. Temperature (°C)
Electrical energy demand ($\Delta G_f$)

- $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2$
- $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$

750ºC – 900ºC

$\Delta G_{\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2} = \Delta G_{\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2}$
Visions for synfuels from electrolysis of steam and carbon dioxide

1. Big wind turbine parks off-shore in the North sea, couple to a large SOEC system producing methane (SNG), which is fed into the existing natural gas net-work in Denmark

2. Large SOEC systems producing DME, synthetic gasoline and diesel in Island, Canada, Greenland, Argentina, Australia ... driven by geothermal energy, hydropower, solar and wind.

3. The target market should be replacement of natural gas and liquid fuels for transportation

4. All the infrastructure exists!!
Efficiency versus costs

If an energy technology is sustainable (CO₂ – neutral), constantly available and environmental friendly, then the energy efficiency is not important in itself. The energy price for the consumer is the only important factor.

The SOC electrolysis – fuel cell cycle-efficiency is maybe 40 %

Efficiency of conversion of fossil fuel in a car: ca. 25 %

Efficiency of production of bio-ethanol??

In spite of this we urgently need all energy technologies, but we should minimize the consumption of fossils as much as possible.
Production of syngas using SOEC

Reaction Schemes:
The overall reaction for the electrolysis of steam plus CO$_2$ is:
\[ \text{H}_2\text{O} + \text{CO}_2 + \text{heat} + \text{electric energy} \rightarrow \text{H}_2 + \text{CO} + \text{O}_2 \quad (1) \]

This is composed of three partial reactions. At the negative electrode:
\[ \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + \text{O}^{2-} \quad (2) \]
\[ \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO} + \text{O}^{2-} \quad (3) \]

and at the positive electrode:
\[ 2 \text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}^- \quad (4) \]
Methane synthesis

- \( \text{CO} + 3 \text{H}_2 \leftrightharpoons \text{CH}_4 + \text{H}_2\text{O} \)
- Ni-based catalysts,
- 190 °C – 450 °C
- 3 MPa
- Using Ni - in principle possible to produce it inside the SOEC, but the temperature is too high, unless we go to much higher pressures
- Other possible catalyst exists
Thermodynamics of methane, steam and carbon dioxide

Methanol and DME synthesis

- \( \text{CO} + 2 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} \)
- \( 2 \text{CO} + 4 \text{H}_2 \rightleftharpoons (\text{CH}_3)_2\text{O} + \text{H}_2\text{O} \)
- A Cu/ZnO-Al2O3 catalyst
- 200 °C - 300 °C
- 4.5 - 6 MPa
- Again the electrolyser should be pressurized
Methane production using SOEC

\[
\begin{align*}
\text{850 C} & \quad \text{H}_2 + \text{CO} \\
+ \quad 2\text{O}^{2-} & \quad \text{H}_2\text{O} + \text{CO}_2 \\
\text{O}_2 & \quad \text{CH}_4 + \text{H}_2\text{O} \\
& \quad \text{O}_2 \quad \text{25 C}
\end{align*}
\]

Heat exchange

Nickel

Heat exchange
Gasoline production using SOEC

Fischer-Tropsch-catalyst

850 °C

H₂ + CO → Gasoline

2O²⁻ → e⁻

H₂O + CO₂ → O₂

Heat exchange

Heat exchange

Heat exchange
SOEC - catalytic reactor integration
Visions for synfuels by electrolysis of steam and CO$_2$

1. Wind turbine parks off-shore in the North sea, couple to a large SOEC system producing CH$_4$ fed into the natural gas pipe lines.

2. Large SOEC systems producing DME, synthetic gasoline and diesel in Island, Canada, Greenland ... driven by geothermal energy and hydropower. Danish companies might build and own these factories.

3. The target market should be replacement of natural gas and liquid fuels for transportation.

4. All the infrastructure exists!!
Conversion of renewable power

**Production of fuel:**
- **Catalysis:** CH₄ or CH₃OH
- **Electrolysis:** CO + H₂

**Consumption:** Fuel cell or Otto engine

**Energy Sources:**
- Electricity from wind or water
- CO₂ from the atmosphere
- H₂O from wind or water

**Chemical Reactions:**
- Ca(OH)₂ + CO₂ (from air) ➔ CaCO₃ + H₂O
- CaO + H₂O ➔ Ca(OH)₂ + heat
- CaCO₃ + heat ➔ CaO + CO₂
- CaO + CO₂ ➔ CaCO₃ + heat
- Ca(OH)₂ + CO₂ (from air) ➔ CaCO₃ + H₂O
- CaO + H₂O ➔ Ca(OH)₂ + heat
## Possible energy carries

<table>
<thead>
<tr>
<th>Type</th>
<th>MJ/l</th>
<th>MJ/kg</th>
<th>Boiling °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>33</td>
<td>46</td>
<td>40 - 200</td>
</tr>
<tr>
<td>Diesel</td>
<td>38</td>
<td>46</td>
<td>130 - 400</td>
</tr>
<tr>
<td>Liquid methane</td>
<td>24</td>
<td>56</td>
<td>-162</td>
</tr>
<tr>
<td>LPG</td>
<td>27</td>
<td>50</td>
<td>-42 - 0</td>
</tr>
<tr>
<td>DME = (CH₃)₂O</td>
<td>22</td>
<td>30</td>
<td>-25</td>
</tr>
<tr>
<td>Methanol</td>
<td>18</td>
<td>23</td>
<td>65</td>
</tr>
<tr>
<td>Ethanol</td>
<td>24</td>
<td>30</td>
<td>78</td>
</tr>
<tr>
<td>Bio diesel</td>
<td>33</td>
<td>40</td>
<td>180 - 340</td>
</tr>
<tr>
<td>Liquid ammonia</td>
<td>33</td>
<td>25</td>
<td>-33</td>
</tr>
</tbody>
</table>
Which fuel is preferable?

Gas:
1. SNG = CH₄

Liquids:
1. DME = CH₃OCH₃ (a gas, easy to liquefy)
2. Methanol = CH₃OH, poisonous, soluble in water
3. Synthetic diesel and gasoline (Fischer Tropsch), more expensive to synthesize than those above

Each of them has pros and cons, but SNG and DME are my favorites
First conclusion

There is probably a need for all kinds of energy conversion and storage technology in the future, but

The reversible SOC combined with catalytic reactors for SNG or liquid hydrocarbons is the one we need the most

😊

So what have we been doing so far?

(The Risø DTU SOC state of the art is reasonably typical for the international state of the art, and therefore, the Risø DTU - Topsoe Fuels Cells technology is used as example).
From cells to stacks

• Each fuel cell gives a voltage of ~ 0.8 volt. To attain useful voltages several cells, e.g. 50, are stacked in series.

• High energy density: Stack electric power density of 2.5 kW/liter demonstrated with by Topsoe - Risø DTU cell stacks.

• Scalable technology: From kW to MW.
Danish SOFC consortium

• Risø DTU
  • R&D – from fundamental aspects to technology (since 1989)
  • Pre-pilot plant for cell production
  • Test and evaluation

• Topsoe Fuel Cell A/S
  • Stack technology
  • Cell and stack manufacturing
  • System design
  • Commercialization
New Topsoe Fuel Cell pilot plant

- Inaugurated spring 2009
- Production for development, test and market introduction
- 5 MW per year capacity (for demos)
- Full scale plant in 3-5 years
SOFC performance

$i$ - $V$ and $i$ - $P$ curves for a Risø SOFC anode supported Ni-YSZ/YSZ/CGO/LSC-CGO cell. Max $P = 15$ kW/m$^2$
Cell performance

World record!

$V - i$ curves for a Ni-YSZ-supported Ni/YSZ/LSM SOEC: electrolyzer (negative cd) and fuel cell (positive cd) at different temperatures and steam or CO$_2$ partial pressures - balance is H$_2$ or CO.

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The pressure test setup
Durability

- The durability of both Ni-YSZ-LSM cells and Ni-YSZ-LSFC has been solved (close to zero degradation in stacks) for less than 0.5 Acm\(^{-2}\) and temperature higher than 750 °C (LSM) or 700 °C (LSCF) in SOFC mode on stack level. If gases are very clean then possibly OK at higher c.d. and lower temperature. Under test.

- Similar results obtained in SOEC mode, where impurities are even more important as explained next
Topsoe stack test with Risø Ni-YSZ/YSZ/CGO/LSFC 2.5G cells

Durability test of a 10 cell stack with 12x12 cm² 2.5G cells and coated metallic interconnects. 750 °C and 0.22 A/cm². Gases not extra cleaned.

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**CO₂ electrolysis - impurities**

850 °C, 0.25 A/cm²

* The increase in cell voltage after 295 and 363 hours of electrolysis was caused by a sensor break in the oven temperature control causing a lowering of the cell temperature to 795°C and 835°C respectively.

Degradation from 25 - 600 h: 1 mV / 1000 h

- CO₂ - CO as provided
- Clean CO₂ - CO

Sune Ebbesen and Mogens Mogensen, patent application filed.
Data in ESSL, 2010

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Co-electrolysis of H$_2$O and CO$_2$

1 kW - 10-cell stack – 12×12 cm$^2$

850 ºC, -0.50 A/cm$^2$ or -0.75 A/cm$^2$, 45 % CO$_2$ / 45% H$_2$O / 10 % H$_2$

S. Ebbesen et al. submitted
Degradation at high c.d.

Test A: -2.0 A·cm⁻², B: -1.5 A·cm⁻² and C: -1.0 A·cm⁻² operated at 850 °C with 50:50 H₂O:H₂

Ruth Knibbe et al., JES, 157 (2010) B1209
Degradation at high c.d.

- Much smaller $R_p$ than $R_s$ degradation
- TEM reveals that it is due to $O_2$ bubble precipitation inside the electrolyte near the $O_2$ LSM/YSZ-electrode destroying $\sigma_{O_2^-}$. 

![TEM Image](image_url)
Problems

• We have had problems – some are solved – but we still have many problems

• As it was just shown, we still have durability at high power problems to be solved, and we certainly have a lot more that may be optimized

• As usual with new technologies the cost reduction is the main problem. The way we deal with it is to: 1) bring down the ASR, 2) extend the life time at high current densities (above 2 A cm\(^{-2}\)), and 3) improve the thermo-mechanical reliability

Some economic estimates follows:
Economy assumptions for H₂ production using SOEC

<table>
<thead>
<tr>
<th>Assumption</th>
<th>Value</th>
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<tbody>
<tr>
<td>Electricity</td>
<td>1.3 US¢/kWh</td>
</tr>
<tr>
<td>Heat</td>
<td>0.3 US¢/kWh</td>
</tr>
<tr>
<td>Investment</td>
<td>4000 $/m² cell area</td>
</tr>
<tr>
<td>Demineralised Water</td>
<td>2.3 $/m³</td>
</tr>
<tr>
<td>Cell temperature</td>
<td>850 °C</td>
</tr>
<tr>
<td>Heat reservoir temperature</td>
<td>110 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>1 atm</td>
</tr>
<tr>
<td>Cell voltage</td>
<td>1.29 V (thermo neutral potential)</td>
</tr>
<tr>
<td>Life time</td>
<td>10 years.</td>
</tr>
<tr>
<td>Operating activity</td>
<td>50%</td>
</tr>
<tr>
<td>Interest rate</td>
<td>5%</td>
</tr>
<tr>
<td>Energy loss in heat exchanger</td>
<td>5%</td>
</tr>
<tr>
<td>H₂O inlet concentration</td>
<td>95% (5% H₂)</td>
</tr>
<tr>
<td>H₂O outlet concentration</td>
<td>5% (95% H₂)</td>
</tr>
</tbody>
</table>
H₂ production – economy estimation

* Conversion of H₂ to equivalent crude oil price is on a pure energy content (J/kg) basis

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### Economy assumptions for CO production by SOEC

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Electricity</td>
<td>1.3 US¢/kWh</td>
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<tr>
<td>Heat</td>
<td>0.3 US¢/kWh</td>
</tr>
<tr>
<td>Investment</td>
<td>4000 $/m² cell area</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>2.3 $/ton</td>
</tr>
<tr>
<td>Cell temperature</td>
<td>850 ° C</td>
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<tr>
<td>Heat reservoir temperature</td>
<td>110 ° C</td>
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<tr>
<td>Pressure</td>
<td>1 atm</td>
</tr>
<tr>
<td>Cell voltage*</td>
<td>1.47 V (thermo neutral potential)</td>
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<tr>
<td>Life time</td>
<td>10 years.</td>
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<tr>
<td>Operating activity</td>
<td>50%</td>
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<tr>
<td>Interest rate</td>
<td>5%</td>
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<tr>
<td>Energy loss in heat exchanger</td>
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<td>( \text{CO}_2 ) inlet concentration</td>
<td>95% (5% CO)</td>
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<tr>
<td>( \text{CO}_2 ) outlet concentration</td>
<td>5% (95% CO)</td>
</tr>
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</table>
CO production – economy estimation

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

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Concluding remarks

• Durability of the cell at high current density (2 - 4 A/cm²) must be improved

• Pressurized operation to be developed – first tests at 10 bar done

• Costs should be further decreased

• A most efficient way of cost reduction is further reduction of the internal resistance of the SOC: ½ resistance → 2 power input at a given voltage - the thermo-neutral voltage usually

• Materials costs have to be reduced

• Efficiency is not important on its own - only cost is. There is enough energy delivered from the sun
Acknowledgement

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- EU
- Topsoe Fuel Cell A/S
- Danish Programme Committee for Energy and Environment
- Danish Programme Committee for Nano Science and Technology, Biotechnology and IT

and the work of many colleagues over the years.