Production of Synthetic Fuel by Electrolysis: Potential and Challenges

Mogens Mogensen

Fuel Cells and Solid State Chemistry Division
Risø National lab for Sustainable Energy
Technical University of Denmark
Roskilde, Denmark

Workshop on Sustainable Fuels from CO₂, H₂O and Carbon-Free Energy
Columbia University, New York, May 4, 2010
Outline

- Motivation for synthetic hydrocarbons
- Technical possibilities
- Principle of SOEC
- Efficiency
- Which type of fuel?
- When?
- Outlook
## Motivation 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>46</td>
<td>40 - 200</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>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li-ion batteries</td>
<td>0.5 - 1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Motivation 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 100 kg battery package (1 MJ/kg) this means a power of ca. 3.5 kW i.e. it takes 8 h to get 100 MJ on board.

• The ratio between the driving range is only ca. a factor of 5, because the electric engine has about an efficiency of 80 % while the gasoline engine has ca. 25 %.
CO₂ + H₂O electrolysis - Possibilities

Several possibilities for electrolyte exist:

1. Low temperature “solid” proton conductor (PEM), 70 – 90 °C, very expensive (and only one paper on CO₂)

2. Simple aqueous electrolyte (e.g. K₂CO₃) solution (lower than 100 °C)

3. Immobilized aqueous K₂CO₃, Na₂CO₃ etc in mesoporous ceramic structures (e.g. SrTiO₃) – pressurized, 200 – 300 (400) °C

4. Solid acids, 200 – 250 °C

5. High temperature solid oxide ion conductor (stabilized zirconia), 750 – 950 °C
CO$_2$ reduction at RT

Variation of the Faradaic efficiencies of the products in electrochemical reduction of CO, obtained in controlled potential electrolysis, 0.1 mol dm$^{-3}$ KHCO$_3$, at 19 °C.

CO₂ reduction at RT

• In order to have a chance to make commercial CO₂ electrolysis, a current density of say more than 1 A cm⁻² at -0.8 to -1.0 V vs NHE and with more than 80% yield is necessary.
• Thus, the results of Hori et al. of 5 mA cm⁻² at -1.5 V vs NHE and a yield of CH₄ of ca. 45% is very far from the goal.
• Totally new improved electrocatalysts are necessary. Some of our cooperators are working on this.

• Risø DTU has started activities on CO₂ reduction in the temperature range 200 – 300 °C, pressure 50 -100 bar (ACEC = aqueous carbonate electrolyser cell), but no results yet.
• We have a record in CO₂ reduction using SOEC – 750 – 950 °C.
Why ACEC = electrolysis below 300 °C

• Electrolysis of H₂O & CO₂ into hydrocarbon, ether or alcohol are moderately endothermic or exothermic.

• Thus, if we can speed up the electrochemical reaction rate sufficiently by high pressure and improved electrocatalysts, then this may eventually be most favorable. The lower temperature and only an electrolysis unit (no catalytic reactor) open up for small decentralized applications.
Why SOEC = electrolysis at high temperature?

• Only SOEC has been proven practical – yet not commercialized

• Electrolysis of H₂O & CO₂ into H₂ & CO are heat consuming processes. The Joule heat contributes to the splitting of the water and CO₂ molecules. Thus, the higher the temperature, the less electrical energy is need for the splitting.

• The rate of the electrochemical processes is much faster at high temperature. More m³ H₂ per m² cell per minute gives lower investment costs.

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

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

Current collector, LSM, \(\sim 40\mu m\)

Active oxygen electrode layer, LSM/YSZ, \(\sim 20\mu m\)

Electrolyte, YSZ, \(\sim 10\mu m\)

Active hydrogen/CO electrode layer, Ni/YSZ, \(\sim 15\mu m\)

Current collector (support), Ni/YSZ, \(\sim 250\mu m\)

\[\text{LSM} = (\text{La}_{1-x}\text{Sr}_x)_{\text{MnO}_3}\]

\[\text{YSZ} = \text{Zr}_{0.84}\text{Sr}_{0.16}\text{O}_{1.92}\]
Ni - YSZ supported cell

LSM/YSZ electrode

YSZ electrolyte

Ni/YSZ electrode

Ni/YSZ support

10μm

EHT = 5.00 kV
WD = 2 mm

Signal A = InLens
Photo No. = 8322

Date: 31 Oct 2005
Time: 18:02:14
Risø DTU SOCs

Active cell area 4x4 cm$^2$ or 18x18 cm$^2$
Performance of reversible SOC

World record in electrolysis

Thermodynamics

$H_2O \rightarrow H_2 + \frac{1}{2}O_2$

Energy (“volt”) = \frac{\text{Energy (kJ/mol)} }{2F}$
Thermodynamics

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

Total energy demand ($\Delta H_f$)

Energy demand (KJ/mol)

Temperature (°C)

Energy demand (Volt)
Thermodynamics

Electrical energy demand ($\Delta G_f$)

Energy demand (KJ/mol)

Temperature ($^\circ$C)

\[ \Delta G_{\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2} = \Delta G_{\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2} \]

750$^\circ$C – 900$^\circ$C

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

H$_2$O $\rightarrow$ H$_2$ + $\frac{1}{2}$O$_2$
Efficiency versus costs

If an energy technology is sustainable (CO$_2$ – 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: 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:

\[ \text{H}_2\text{O} + \text{CO}_2 + \text{heat} + \text{electric energy} \rightarrow \text{H}_2 + \text{CO} + \text{O}_2 \]  

(1)

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

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

(2)

\[ \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO} + \text{O}^{2-} \]  

(3)

and at the positive electrode:

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

(4)
Methane synthesis

- $\text{CO} + 3 \text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$
- Ni-based catalysts,
- $190 \, ^\circ\text{C} - 450 \, ^\circ\text{C}$
- 3 MPa

- Using Ni - in principle possible to produce it inside the SOEC, but the temperature is too low, unless we go to much higher pressures

- Other possible catalyst exists
Thermodynamics of methane, steam and carbon dioxide

Methanol and DME synthesis

• CO + 2 H₂ ⇌ CH₃OH

• 2 CO + 4 H₂ ⇌ (CH₃)₂O + H₂O

• A Cu/ZnO-Al₂O₃ catalyst

• 200 °C - 300 °C

• 4.5 - 6 MPa

• Again the electrolyser should be pressurized
Methane production using SOEC

\[ \text{850°C} + 2\text{O}_2^- \rightarrow \text{H}_2 + \text{CO} \quad \rightarrow \quad \text{H}_2\text{O} + \text{CO}_2 \]

\[ + \quad 400°C \quad \text{Heat exchange} \quad \rightarrow \quad \text{CH}_4 + \text{H}_2\text{O} \quad \rightarrow \quad \text{H}_2\text{O} + \text{CO}_2 \]

\[ \text{O}_2 \quad \rightarrow \quad \text{Heat exchange} \quad \rightarrow \quad \text{O}_2 \]

Nickel
Gasoline production using SOEC

Fischer-Tropsch-catalyst

850°C

H₂ + CO

H₂O + CO₂

O₂

25°C

25°C

Heat exchange

Heat exchange

Gasoline

O₂
Danish 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

Consumption: Fuel cell or Otto engine

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

Power

H₂O into the atmosphere

Transport

Electricity from wind or water

CO₂ into the atmosphere

H₂O

Ca(OH)₂ + CO₂ (from air) →
CaCO₃ + H₂O

CaO + H₂O →
Ca(OH)₂ + heat

CaCO₃ + heat →
CaO + CO₂

CaO + H₂O

CO₂

H₂O
### 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 (an easy to liquefy gas)
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
Outlook
Problems

• Durability of the H₂O- and the CO₂-electrode at high current density (2 - 4 A/cm²) must be improved

• Redox tolerant Ni-YSZ-electrode or all ceramic cathode (H₂O, CO₂) should be developed

• Costs should be further decreased

• Pressurized operation to be further developed

• A most efficient way of cost reduction is further reduction of area specific resistance of the SOEC
Acknowledgement

We gratefully acknowledge support from our sponsors:

- Danish Programme Committee for Energy and Environment
- Danish National Advanced Technology Foundation
- Energinet.dk (Danish electric grid owner)
- European Union

Thank you for your attention!