Co-Electrolysis of Water and CO2 for synthetic fuels

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Co-Electrolysis of Water and CO₂ for synthetic fuels

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Outline

1. Solid Oxide Electrolyser Cell (SOEC)

2. SOEC Electrode Potentials, Thermodynamic

3. Gas Diffusion and Conversion
The Solid Oxide Cell
The Solid Oxide Cell

Ni-YSZ support & current collector

Ni-YSZ electrode

YSZ electrolyte

LSM-YSZ electrode

LSM current collector

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

YSZ = Zr$_{0.84}$Y$_{0.16}$O$_{1.92}$
The Solid Oxide Cell

Solid Oxide Electrolysis Cell

H₂O (and CO₂) → H₂ (and CO) + O₂

1.3 V

Solid Oxide Fuel Cell

O₂ → H₂ (and CO) + H₂O (and CO₂)

0.8 V

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The Solid Oxide Cell

Cell voltage $V$ [V] vs. Current density $i$ [A/cm$^2$]

- 950°C, 70% CO$_2$
- 950°C, 70% H$_2$O
- 850°C, 50% H$_2$O
- 750°C, 50% H$_2$O

SOFC

SOEC

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Thermodynamics

\[ H_2O \rightarrow H_2 + \frac{1}{2}O_2 \]

Energy demand (KJ/mol)

Electrical energy demand (\(\Delta G_f\))

Heat demand (\(T\Delta S_f\))

\[ \eta = 100\% \text{ at } E = E_{tn} \text{ (no heat loss)} \]
Thermodynamics

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

- Total energy demand (\(\Delta H_f\))
- Electrical energy demand (\(\Delta G_f\))
- Heat demand (\(T\Delta S_f\))

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

**Electrical energy demand ($\Delta G_f$)**

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

At 750°C – 900°C:

$$\Delta G_{\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2} = \Delta G_{\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2}$$
Co-electrolysis of H$_2$O and CO$_2$

1 kW - 10-cell stack – 12 × 12 cm$^2$
850 °C, -0.50 (-0.75) A/cm$^2$, 45 % CO$_2$ / 45% H$_2$O / 10 % H$_2$

S. Ebbesen et al.
Electrolyte degradation at high current


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Electrolyte degradation at high current

TEM of YSZ grain boundary near oxygen electrode from cell tested at -2 A/cm² (R_s increase)

Pore / gaps inbetween YSZ grains in the YSZ close to the electrolyte – oxygen electrode interface observed.
The Pressure Test Setup

Graph: 
- Title: 850 °C, 50% H₂ + 50% H₂O, Air
- Axes:
  - Y-axis: Cell voltage / V
  - X-axis: Current density / A/cm²
- Data points:
  - 1 bar
  - 10 bar

Image: Test setup equipment with tubing and connections.
Synthetic Fuel Production

CO₂ → Purification

H₂O(1) → Recycled

synth. fuel(1) → Catalyst

O₂ →

300 °C

H₂O(g) + CO₂ → CO + H₂ + H₂O(g) + CO₂

SOEC stack

900 °C

O₂
Synthetic Fuel Production Economy

S. D. Ebbesen, S. H. Jensen, A. Hauch and M. Mogensen, to be submitted
Synthetic Fuel Production Economy

S. D. Ebbesen, S. H. Jensen, A. Hauch and M. Mogensen, to be submitted

1.15 €/L Diesel, EU average excluding taxes

DK Electricity Price in 2010

Average Price

Electricity price (¢/kWh)

Hours
SOEC Economy

Søren Højgaard Jensen, Unpublished work
WTI and BRENXT Crude Oil price

WTI

$\text{$/barrel}$

BRENT

$\text{$/barrel}$

Sep08 09 10 11 12 Sep13

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Conclusions

1. Stable co-electrolysis operation below -1 A/cm²

2. Operation at high pressure makes internal catalysis possible which enables high production efficiency

3. Using Only Cheap Electricity Doesn’t change the synthetic fuel production costs significantly
Acknowledgement

I wish to thank Colleagues at DTU Energy Conversion for contributions to this presentation
CO₂ + 2H₂O ⇌ CH₄ + 2O₂

ΔH°

8F = 1.15 V

ΔG°¹⁰⁰⁰⁰⁰C

8F = 1.04 V
At 15 Mpa and 650 C, a mixture of 85% methane and 15% hydrogen dry gas with small concentrations of CO and CO$_2$ can be produced without producing equilibrium carbon, at V = 1.08 V vs. air.

S. H. Jensen and M. Mogensen, 19$^{th}$ World Energy Congress, Sydney, Australia 2004

\[
\begin{align*}
\text{CO}_2 + 2\text{H}_2\text{O} & \leftrightarrow \text{CH}_4 + 2\text{O}_2 \\
\frac{\Delta H^0}{8F} & = 1.15 \text{ V} \\
\frac{\Delta G^{1000\text{C}}}{8F} & = 1.04 \text{ V}
\end{align*}
\]
Vision

Ll. Thorup Salt caverns

- 150-200 bar
- 500 mill Nm$^3$ storage
- 5000 mill kWh stored
- 200 M€ CAPEX
## Vision

<table>
<thead>
<tr>
<th>Operating cost and conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating pressure</td>
<td>150-200 bar</td>
</tr>
<tr>
<td>Storage capacity (volume)</td>
<td>500 Mio Nm³</td>
</tr>
<tr>
<td>Storage capacity (Energy (CH₄))</td>
<td>5000 GWh</td>
</tr>
<tr>
<td>Cavern CAPEX (CH₄)</td>
<td>200 M€</td>
</tr>
<tr>
<td>Cavern CAPEX (CO₂ + CH₄)</td>
<td>0.08 €/kWh</td>
</tr>
<tr>
<td>Electrolysis/Fuel-cell operation/year</td>
<td>4000 hours</td>
</tr>
<tr>
<td>SOC cost</td>
<td>150 €/kW</td>
</tr>
<tr>
<td>Total SOC CAPEX</td>
<td>200 M€</td>
</tr>
<tr>
<td>Total system CAPEX</td>
<td>600 M€ (0.12 €/kWh)</td>
</tr>
</tbody>
</table>

Assume the return of investment on the storage facility is 5 years, the round trip efficiency is 70% and that the storage facility buys electricity during the summer (4000 h) at a cost of 9.6 €¢/kWh. Then the storage facility will be able to sell electricity during the winter periods (4000 h) for 14 €¢/kWh.