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

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

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

Solid Oxide Electrolysis Cell

- $\text{H}_2\text{O (and CO}_2\text{)}$ $\rightarrow$ $\text{H}_2$ (and CO)
- $\text{O}_2$ $\rightarrow$ $\text{O}_2$

1.3 V

Solid Oxide Fuel Cell

- $\text{O}_2$ $\rightarrow$ $\text{H}_2$ (and CO)
- $\text{H}_2\text{O (and CO}_2\text{)}$ $\rightarrow$ $\text{H}_2\text{O (and CO}_2\text{)}$

0.8 V

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

Total energy demand ($\Delta H_f$)

Electrical energy demand ($\Delta G_f$)

Heat demand ($T\Delta S_f$)

$\eta = 100\%$ at $E = E_{tn}$ (no heat loss)
CO₂ → CO + ½O₂

Total energy demand (ΔHᵣ)

Electrical energy demand (ΔGᵣ)

Heat demand (TΔSᵣ)

Energy demand (KJ/mol)

Energy demand (Volt)

Temperature (ºC)
Electrical energy demand ($\Delta G_f$)

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

$750^\circ\text{C} - 900^\circ\text{C}$

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

1 kW - 10-cell stack – $12 \times 12 \text{ cm}^2$
850 °C, -0.50 (-0.75) A/cm$^2$, 45% CO$^2$ / 45% H$\text{2O}$ / 10% H$\text{2}$

S. Ebbesen et al.
Electrolyte degradation at high current

Ref. Knibbe et al., J. Electrochem. Soc., 157(8), B1209, 2010

DTU Energy Conversion, Technical University of Denmark
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 in between YSZ grains in the YSZ close to the electrolyte – oxygen electrode interface observed.
The Pressure Test Setup

850°C, 50% H₂ + 50% H₂O, Air

Cell voltage / V

Current density / A/cm²

1 bar 10 bar
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\(^1\)

\(^1\)Europe's Energy Portal. [http://www.energy.eu](http://www.energy.eu) . 2013
DK Electricity Price in 2010

Average Price
SOEC Economy

Søren Højgaard Jensen, Unpublished work

DTU Energy Conversion, Technical University of Denmark
WTI and BRENT Crude Oil price

WTI

BRENT

$/barrel

DTU Energy Conversion, Technical University of Denmark
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
I wish to thank Colleagues at DTU Energy Conversion for contributions to this presentation.
Vision

\[ \text{CO}_2 + 2\text{H}_2\text{O} \leftrightarrow \text{CH}_4 + 2\text{O}_2 \]

\[
\frac{\Delta H^0}{8F} = 1.15 \text{ V}
\]

\[
\frac{\Delta G^{1000^\circ C}}{8F} = 1.04 \text{ V}
\]
At 15 Mpa and 650 °C, a mixture of 85% methane and 15% hydrogen dry gas with small concentrations of CO and CO₂ can be produced without producing equilibrium carbon, at V= 1.08 V vs. air.

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

\[
\text{CO}_2 + 2\text{H}_2\text{O} \leftrightarrow \text{CH}_4 + 2\text{O}_2
\]

\[
\frac{\Delta H^o}{8F} = 1.15 \text{ V}
\]

\[
\frac{\Delta G^{1000^\circ C}}{8F} = 1.04 \text{ V}
\]
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>
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<tbody>
<tr>
<td>Operating pressure</td>
<td>150-200 bar</td>
</tr>
<tr>
<td>Storage capacity (volume)</td>
<td>500 Mio Nm$^3$</td>
</tr>
<tr>
<td>Storage capacity (Energy (CH$_4$))</td>
<td>5000 GWh</td>
</tr>
<tr>
<td>Cavern CAPEX (CH$_4$)</td>
<td>200 M€</td>
</tr>
<tr>
<td>Cavern CAPEX (CO$_2$ + CH$_4$)</td>
<td>0.08 €/kWh</td>
</tr>
<tr>
<td>Electrolysis/Fuel-cell operation/year</td>
<td>4000 hours</td>
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<tr>
<td>SOC cost</td>
<td>150 €/kW</td>
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<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.