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

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

$$\text{YSZ} = \text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92}$$

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The Solid Oxide Cell

Solid Oxide Electrolysis Cell

H₂O (and CO₂) → H₂ (and CO) + O₂ (1.3 V)

Solid Oxide Fuel Cell

O₂ → H₂O (and CO₂) (0.8 V)

H₂ (and CO) → H₂O (and CO₂)
The Solid Oxide Cell

- **SOFC**
  - 950 °C, 70% CO₂
- **SOEC**
  - 950 °C, 70% H₂O
  - 850 °C, 50% H₂O
  - 750 °C, 50% H₂O

Cell voltage $V$ [V]

Current density $i$ [A/cm²]
H₂O → H₂ + ½O₂

η = 100 % at E = Eₜₙ (no heat loss)

Eₜₙ = Eₜₙ

Temperature (°C)

Energy demand (KJ/mol)

Liquid

Gas

Total energy demand (ΔHᵣ)

Electrical energy demand (ΔGᵣ)

Heat demand (TΔSᵣ)

1/(2·n·F) · Energy demand (Volt)
CO₂ → CO + \frac{1}{2}O₂

Total energy demand (\Delta H_f)

Electrical energy demand (\Delta G_f)

Heat demand (T\Delta S_f)

Energy demand (KJ/mol)

Temperature (°C)
Electrical energy demand ($\Delta G_f$)

$$\Delta G_{H_2O \rightarrow H_2 + \frac{1}{2}O_2} = \Delta G_{CO_2 \rightarrow CO + \frac{1}{2}O_2}$$

$750^\circ C - 900^\circ C$
Co-electrolysis of H₂O and CO₂

1 kW - 10-cell stack – 12 × 12 cm²
850 °C, -0.50 (-0.75) A/cm², 45 % CO² / 45% H₂O / 10 % H₂

S. Ebbesen et al.
Electrolyte degradation at high current

Cell with $R_s$ constant (-1 A/cm$^2$)

Cell with $R_s$ increase (-2 A/cm$^2$)

TEM study of the YSZ grain boundaries.... →

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

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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

Cell voltage / V

Current density / A/cm²

850 °C, 50% H₂ + 50% H₂O, Air

1 bar 10 bar
Synthetic Fuel Production

\[ \text{CO}_2 \rightarrow \text{Purification} \rightarrow 300 \, ^\circ\text{C} \rightarrow \text{Insulation} \rightarrow 900 \, ^\circ\text{C} \]

\[ \text{H}_2\text{O(l)} \rightarrow \text{Recycling} \rightarrow \text{Catalyst} \]

\[ \text{CO} + \text{H}_2 + \text{H}_2\text{O(g)} + \text{CO}_2 \]

\[ \text{O}_2 \rightarrow \text{SOEC stack} \rightarrow + \]
Electricity price (€¢/kWh) over the years:

- Ireland
- Italy
- EU Average
- Norway
- France
- Finland

Average price: 9.6 €¢/kWh

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

- Hydrogen production price (€/kg \( \text{H}_2 \))
- FT-diesel production price (€/l)

Production price (€)

Electricity price (€/kWh)

1.15 €/L Diesel, EU average excluding taxes¹

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

DK Electricity Price in 2010

Average Price
SOEC Economy

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

WTI

BRENT

$/barrel

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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
I wish to thank Colleagues at DTU Energy Conversion for contributions to this presentation
CO$_2$+2H$_2$O $\leftrightarrow$ CH$_4$+2O$_2$

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

\[
\frac{\Delta G^{1000\text{C}}}{8F} = 1.04 \text{ V}
\]
At 15 Mpa and 650 C, a mixture of 85% methane and 15% hydrogen dry gas with small concentrations of CO and 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

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

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

$$\frac{\Delta G^{1000\text{C}}}{8F} = 1.04 \text{ V}$$
Vision

LL. Thorup Salt caverns

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