Co-Electrolysis of Water and CO2 for synthetic fuels

Jensen, Søren Højgaard

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Co-Electrolysis of Water and CO$_2$ for synthetic fuels

Søren Højgaard Jensen
Technical University of Denmark,
DTU Risø Campus
DK-4000 Roskilde
Denmark

shjj@dtu.dk
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

LSM = \((\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{MnO}_3\)  
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 → H₂ (and CO) + H₂O (and CO₂)

0.8 V

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

\[ \text{E}_{\text{cell}} = \text{E}_{tn} \]
CO$_2$ $\rightarrow$ CO + $\frac{1}{2}$O$_2$

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

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

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

- Energy demand (kJ/mol)
- Temperature (°C)
- Energy demand (Volt)
**Thermodynamics**

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

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

**Equation**

$$\Delta G_{\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2} = \Delta G_{\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2}$$
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 % $\text{CO}_2$ / 45% $\text{H}_2\text{O}$ / 10 % $\text{H}_2$

S. Ebbesen et al.
Electrolyte degradation at high current

Cell with $R_s$ constant
(-1 A/cm²)

Cell with $R_s$ increase
(-2 A/cm²)

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

850 °C, 50% H₂ + 50% H₂O, Air

Cell voltage / V

Current density / A/cm²

1 bar 10 bar
Synthetic Fuel Production

CO₂ → Purification → H₂O(l) → synth. fuel(l) → O₂

300 °C

Insulation

H₂O(g) + CO₂ + H₂ + CO → CO + H₂ + H₂O(g) + CO₂

900 °C

SOEC stack

Catalyst

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Synthetic Fuel Production Economy

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

- Hydrogen production price (€/kg H₂)
- FT-diesel production price (€/l)

SOEC - 0.25 A/cm²
- 74% Electricity
- 24% Investment cost
- 2% Other cost

SOEC - 1.00 A/cm²
- 91% Electricity
- 7% Investment cost
- 2% Other cost

1.15 €/L Diesel, EU average excluding taxes


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

- DK Electricity Price in 2010
- Average Price

Electricity price (¢/kWh) vs. Hours
SOEC Economy

Søren Højgaard Jensen, Unpublished work

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

WTI

$/barrel

BRENT

$/barrel

Sep08 09 10 11 12 Sep13

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
I wish to thank Colleagues at DTU Energy Conversion for contributions to this presentation
Vision

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

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

\[ \Delta G^{1000^\circ\text{C}} \]

\[ \frac{8F}{8F} = 1.04 \text{ V} \]
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

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

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

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

LI. 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.