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

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

Solid Oxide Electrolysis Cell

+ \rightarrow \text{O}_2 \quad 1.3 \text{ V}

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

Solid Oxide Fuel Cell

\text{O}_2 \quad \rightarrow \quad +

\text{H}_2 \text{ (and CO)} \quad \rightarrow \quad \text{H}_2 \text{O (and CO}_2) \quad 0.8 \text{ V}

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The Solid Oxide Cell

SOFC

SOEC

Cell voltage $V$ [V]

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

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Thermodynamics

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

Energy demand (KJ/mol)

\( E_{\text{cell}} = E_{\text{tn}} \)

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

Total energy demand (∆Hᵣ)

Electrical energy demand (∆Gᵣ)

Heat demand (T∆Sᵣ)

Energy demand (KJ/mol)

Energy demand (Volt)

Temperature (°C)

Thermodynamics
Thermodynamics

Electrical energy demand ($\Delta G_f$)

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

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

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 ºC, -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

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

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 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

\[
\begin{align*}
\text{CO}_2 & \rightarrow \text{Purification} \\
\text{H}_2\text{O(l)} & \rightarrow \\
\text{synth. fuel(l)} & \rightarrow \\
\text{O}_2 & \rightarrow
\end{align*}
\]

300 °C

\[
\begin{align*}
\text{H}_2\text{O(g)} + \text{CO}_2 & \rightarrow \text{H}_2 + \text{CO} \\
\text{CO} + \text{H}_2 + \text{H}_2\text{O(g)} & \rightarrow \text{CO}_2
\end{align*}
\]

Insulation

900 °C

SOEC stack

O_2
Synthetic Fuel Production Economy

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

Production price (€)

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

Electricity price (€/kWh)

1.15 €/L Diesel, EU average excluding taxes$^1$


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

DTU Energy Conversion, Technical University of Denmark
SOC Economy

DK Electricity Price in 2010

Average Price

Electricity price (¢/kWh)

Hours

DTU Energy Conversion, Technical University of Denmark
SOEC Economy

Søren Højgaard Jensen, Unpublished work

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

WTI

$/barrel

Sep08 09 10 11 12 Sep13

BREAT

$/barrel

Sep08 09 10 11 12 Sep13
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
CO₂ + 2H₂O ⇌ CH₄ + 2O₂

\[ \frac{\Delta H^o}{8F} = 1.15 \text{ V} \]
\[ \frac{\Delta G^{1000\text{C}}}{8F} = 1.04 \text{ V} \]
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

CO$_2$+2H$_2$O $\leftrightarrow$ CH$_4$+2O$_2$

$\Delta H^0 \over 8F = 1.15$ V

$\Delta G^{1000^\circ C} \over 8F = 1.04$ 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.