HYDROGEN PRODUCTION FOR FUEL CELLS

E.R. Stobbe

Hydrogen production for fuel cells

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ECN Fuel Cell Technology
Fuel Processing

Content

• Fuel cells
• Fuel cell applications
• Hydrogen production for PEM FC
  - Requirements
  - Desulphurisation
  - Reforming
  - Gas-cleanup
• Conclusions
Role of fossil fuels

- Fossil fuels will cover > 90% of energy in the next decades

Fuel cells
Clean technology

Fuel cell technology and fossil fuels offers:
- High efficiencies
  - reduced fuel consumption and CO₂ emissions
- Reduction of emissions
  - drastic reduction of emissions: soot, PM, NOx, HC’s, CO
Fuel cells
Basic principle

- **Highly efficient** direct electrochemical conversion of fuels to *electrical energy*

\[
\begin{align*}
H_2 & \rightarrow 2H^+ + 2e^- \\
O_2 + 4H^+ + 4e^- & \rightarrow 2H_2O \\
H_2 + \frac{1}{2} O_2 & \rightarrow H_2O
\end{align*}
\]

Fuel cells
2.5 kWe PEMFC Stack
### Fuel cells
#### Overview fuel cell types

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>AFC</th>
<th>DMFC</th>
<th>MCFC</th>
<th>PAFC</th>
<th>PEMFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium hydroxide</td>
<td>AFC</td>
<td>DMFC</td>
<td>MCFC</td>
<td>PAFC</td>
<td>PEMFC</td>
<td>SOFC</td>
</tr>
<tr>
<td>Operating Temperature</td>
<td>60-90°C</td>
<td>60-130°C</td>
<td>650°C</td>
<td>200°C</td>
<td>80°C</td>
<td>800-1,000°C</td>
</tr>
<tr>
<td>Efficiency</td>
<td>45-60%</td>
<td>40%</td>
<td>45-60%</td>
<td>35-40%</td>
<td>40-60%</td>
<td>50-65%</td>
</tr>
<tr>
<td>Typical Electrical Power</td>
<td>Up to 20 kW</td>
<td>&lt; 10 kW</td>
<td>&gt; 1 MW</td>
<td>&gt; 50 kW</td>
<td>Up to 250 kW</td>
<td>&gt; 200 kW</td>
</tr>
<tr>
<td>Possible Applications</td>
<td>Submarines, spacecraft</td>
<td>Portable applications</td>
<td>Power stations</td>
<td>Power stations</td>
<td>Vehicles, small stationary</td>
<td>Power stations</td>
</tr>
</tbody>
</table>

### Fuel Cells
#### Stationary applications

- Combined Heat and Power Generation
- Decentralised Power Generation
- Uninterrupted Power Supply / Backup Power

1. Lowering Primary Fuel use, lowering CO₂ emissions
2. Security of Supply, fuel diversification
3. Prevent upgrading of electricity infrastructure, virtual power plants

![Stationary Power (< 250 kW)](image)

Micro CHP (1-5 kW)
Fuel Cells
Transport applications

1. Lowering of emissions: particles, NOx, CO, CxHy, SOx
2. Lowering of fuel use, decreasing CO₂ emissions
3. Lowering of noise
4. Fuel diversification

Fuel cells
Which (logistic) fuel?

| Hydrogen |
|------------------|------------------|------------------|------------------|
| + Perfect match (PEM)FC |
| + Simple System |
| + Good fit with wind, solar, .. |
| - Problematic storage |
| - Safety issues |
| - No infrastructure |

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \]
Fuel cells
Hydrogen infrastructure

Equivalent of a single service station
Replacing a 10^7 litres of fuel/yr service station

- Central production, and tube trailer (26.10^6 m^3/yr):
  - Results in 36 tube trailers/day
    (compared to one 30 m^3 gasoline truck/day)
- On-site NG-reforming @ 75% efficiency:
  - Annual NG consumption: about 13.10^6 m^3
  - Equivalent to 6500 houses
    (2000 m^3/yr/house)
- On-site electrolysis @ 85% efficiency:
  - Annual electricity use: about 110.10^6 kWh
  - Equivalent to 33.103 houses
    (3300 kWh/yr/house)

On board hydrogen generation from fuels as gasoline, diesel
would simplify fuel retailing

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Fuel cells
Which (logistic) fuel?

Hydrocarbons (gasoline, natural gas, propane, methanol)

| + Existing infrastructure | - Security of supply |
| + Familiar product         | - CO₂ emissions      |
| + Easy handling & storage | - Fuel processing needed |

Hydrocarbons (+) Reformer (+) Hydrogen (+) PEMFC (+)

70-90 °C
H₂+½O₂→H₂O

On board hydrogen generation from fuels as gasoline, diesel
would simplify fuel retailing
Hydrogen production for fuel cells
Integration of fuel processor/ PEM fuel cell

Fuel processing for fuel cells
Specific targets

- Small size and low weight
- Low costs
- Fast load changes
- Fast and safe startup/shut down
Fuel processing for fuel cells

Targets for automotive fuel processors

50kWe Fuel Processor (DOE/FreedomCAR)

<table>
<thead>
<tr>
<th></th>
<th>ATR</th>
<th>WGS</th>
<th>PrOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>GHSV (hr⁻¹)</td>
<td>200.000</td>
<td>30.000</td>
<td>150.000</td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>99.9</td>
<td>90</td>
<td>99.8</td>
</tr>
<tr>
<td>Vol (L/50kWe)</td>
<td>0.65</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Costa ($/kWe)</td>
<td>5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Durability (hr)</td>
<td>5000</td>
<td>5000</td>
<td>5000</td>
</tr>
</tbody>
</table>

*Based on 500,000 units/yr

Targets for total fuel processor system:
- Volume: 65 L (75L)
- Costs: 500$ (3250$)
- Lifetime: 5000 hrs (1000 hrs)

Fuel processing for fuel cells

- Small size and low weight
- Low costs
- Fast load changes
- Fast and safe startup/shut down
- High turn-down ratio’s
- Long lifetime (5,000/50,000 hrs)
- Frequent temperature cycles
- Fuel and air only available gases
- Low pressure (0-few barg)

*New challenges for hydrogen production for processes, catalysts and reactors*
**Fuel processing for fuel cells**

**Desulphurisation**

- Fuel processing and fuel cell catalysts highly sensitive to S: Deep desulphurisation needed
- Targets: Fuel 100 ppb; Hydrogen <10 ppb
- Classical process:
  - HDS (30 bar H2, 300°C) followed by H2S-removal
- Fuel cells:
  - Ambient T and P absorbents for organosulphur compounds without need for H2
**Fuel processing for fuel cells**

**Desulphurisation natural gas**

- NG contains 18 mg/m³ (5ppm) THT as odorant
- Classical absorbent: Activated carbon
- New absorbents: tailor made materials (e.g. Cu/Cr promoted materials, zeolites)

![Sorption volume (litre) required for 1200 m³ NG/yr](image)

**Fuel processing for fuel cells**

**Desulfurisation gasoline/jet fuel/diesel**

- High sulphur fuels (>50 ppm):
  - Regenerative absorption
  - Integrated (Low pressure) HDS/ZnO (large scale applications (MW) only)

- Low sulphur fuels (<50 ppm)
  - "pre-reforming" S absorption
  - "After-reformer" S absorption combined with S tolerant reforming catalysts

- Development of S-specific absorbents in (early) developmental stage; breakthroughs needed!
Fuel processing for fuel cells

**Reforming**

Steam reforming

\[ \text{C}_3\text{H}_8 + 3 \text{H}_2\text{O} \rightarrow 3 \text{ CO} + 7 \text{ H}_2 \]  
-230 kJ/mol

(Catalytic) partial oxidation (CPO)

\[ \text{C}_3\text{H}_8 + 1.5 \text{ O}_2 \rightarrow 3 \text{ CO} + 4 \text{ H}_2 \]  
-230 kJ/mol

Autothermal reforming

\[ \text{C}_3\text{H}_8 + 1.25 \text{ O}_2 + 0.5 \text{ H}_2\text{O} \rightarrow 3\text{CO} + 4.5 \text{ H}_2 \]  
-110 kJ/mol

**Autothermal reforming optimum balance**

- Compactness
- Fast startup / load variations
- System efficiency
Fuel processing for fuel cells
Autothermal reforming

Main issues ATR development

- Catalyst and materials
  - High catalyst activity
  - Low light off
  - Limited availability of steam: low S/C
  - Low O₂/C ratio operation / high preheat
  - Suppression of coke formation
  - Catalyst lifetime (hrs, cycles)
  - Increasing complexity heavier fuels (aromatics, sulphur)

- Reactor
  - Mixing/ pre-heating/pre-ignition
  - Fast start-up
  - Heat integration: compact heat exchangers, steam generation, fuel evaporation and preheating

Reformer catalyst material selection

1. Noble metal for hydrocarbon activation (high activity)
   Rh, Pt, Rh, Ru….

2. Oxide support for (additional) oxygen supply, coke removal, low light off
   Fluorites (ZrO₂, CeO₂, CeZrOₓ)
   Perovkites

\[ egin{align*}
  &\text{CH}_4 \\
  &\rightarrow 2\text{H}_2 + \text{CH}_n,\text{ad} + \text{O}_2 + \text{O}_2 \rightarrow 2\text{O}_2,\text{ad} \\
  &\text{H}_{\text{ad}} + \text{CH}_{\text{ad}} + \text{O}_{\text{ad}} \rightarrow \text{CO} \\
  &\text{O}_2 \rightarrow 2\text{O}_{\text{ad}} \end{align*} \]
Fuel processing for fuel cells
Autothermal reforming

Reformer catalyst material screening:
Oxide support plus 1 w/o Rh: Activity for Propane ATR (S/C=0.5, O₂/C=0.5)

Stability test propane-ATR
Yield \(((\text{CO} + \text{H₂})/\text{input C})\) vs runtime

Stable operation Rh/CeZrO₂ catalyst
GHSV~120000 hr⁻¹
Fuel processing for fuel cells
Autothermal reforming

• Reforming CH₄ and light HC’s well proven (long lifetime, high activity)

• Current and future issues:
  Stable reforming “heavy” logistic fuels for automotive, marine and aircraft applications
  Gasoline, (marine) diesel, kerosene
  High aromatics content
  High sulphur content

Fuel processing for fuel cells
Water gas shift

• Classical approach: two step HTS-LTS

- Fe₃O₄/Cr₂O₃
  Robust but low activity

- Cu/ZnO
  • High activity but limited temperature range (250 °C)
  • Highly pyrophoric

New reactors?
New catalysts?
Fuel processing for fuel cells
Water gas shift

Microflow HTS catalyst: Simulated HTS feed gas

Strategy:
• Highest possible T
• Keep away from equilibrium

Fuel processing for fuel cells
Water gas shift

Adiabatic trajectory
Ideal trajectory
Multi bed
Fuel processing for fuel cells
Water gas shift

• Multibed results (10 kWth)
• Amount of FeCr catalyst reduced from 2 kg to 0.75 kg
• Response time (50-100%) reduced 16 min to <4 min
• However: large penalty due to thermal mass reactor

• Advanced design:
  • Further (drastic) reduction of thermal mass reactor
  • Proper distribution of HTS and LTS conversion
  • Catalyst weight <0.3 kg
  • Response time <2.5 min

Reactor design not sufficient for necessary weight and volume reduction: alternative catalysts needed
Fuel processing for fuel cells

**Water gas shift**

- Water gas shift sections can be reduced dramatically in size/weight by using new WGS catalysts
- New WGS catalyst do not require special in situ pre-treatments and are non-pyrophoric: Startup/shut down simplified and safe operation

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Fuel processing for fuel cells

**CO removal : PrOx**

- Water-gas shift section contains 0.2-0.8 vol% CO while PEM tolerates <50 ppm CO
- Deep CO removal needed
- Options:
  - Selective methanation
  - *Preferential oxidation of CO in the presence of hydrogen*
Fuel processing for fuel cells
CO removal: PrOx

80-250 °C

\[ CO + \frac{1}{2}O_2 \rightarrow CO_2 \quad \Delta H = -283 \text{ kJ/mol} \]

\[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \Delta H = -286 \text{ kJ/mol} \]

Issues:

- Oxidation of CO while preventing oxidation of H₂
- Catalyst stability
- Temperature control
- Reverse Water Gas Shift

Alumina supported Ru/Pt catalyst:

0.5% CO, 10 ppm CO, 0.5% O₂, 19% CO₂, 37% H₂, 15% H₂O, 28% N₂
Fuel Processing
Preferential CO-oxidation

Microreactor with in-built cooling function and temperature profile

Designed to accept two counter-flows:
- PrOx gas @ 250°C
- Fuel Cell Exhaust @ 60°C

Under operating conditions, temperature gradient of 170 to 140°C across the catalyst bed

Fuel Processing
Preferential CO-oxidation

Total flow: 4L/min
Reactor Size: ~20cm³

0.4%CO
0.5%O₂
19%CO₂
40%H₂
20%H₂O
20% N₂
Fuel processing for fuel cells

Conclusions

• Fuel cells offer clean technology for conversion of hydrogen and fossil fuels
• Fuel cell development has driven the development of new solutions for hydrogen production
  - Absorption processes for S removal
  - ATR of CH₄ and higher hydrocarbons
  - Alternative catalytic WGS setup
  - Preferential oxidation as CO cleanup
  - Use of micro reactors
• Current challenges: Make fuel cell systems work on heavy logistic fuels (e.g. kerosene, diesel)