Ammonia: The Key to a Hydrogen Economy

Ammonia Fuel Cell Systems

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• Introduction to Fuel Cells
  ▪ Characteristics
  ▪ Fuel Cell Types
  ▪ Fueling the Fuel Cell

• Ammonia Fuel Cells
  ▪ Advantages and Challenges
  ▪ Direct vs. Reformed NH₃
  ▪ Other Electrochemical Applications

• High Temperature Fuel Cell Focus
  ▪ Ammonia and Solid Oxide Fuel Cells
  ▪ Protonic Ceramic Fuel Cells
The Fuel Cell

FIRST, hydrogen is stripped away from hydrocarbon fuel by steam and catalysts.

NEXT, the hydrogen ions pass through a special membrane; electrons can't go through and are diverted to an electrical circuit where they provide power.

FINALLY, the hydrogen recombines with oxygen from air to make water. The process also releases heat.

(Lamar University)
Fuel Cell Anatomy

- **Fuel Cell Electrodes**
  - Anode (oxidation)
  - Cathode (reduction)

- **Electrocatalyst**
  - Porous, electrically conductive
  - Cost depends on cell temperature

- **Ionic Membrane**
  - Not electrically conductive
  - Protonic or anionic

Fuel cell operating with air/ hydrocarbon feed
Types of Fuel Cells

- Polymer Electrolyte Membrane Fuel Cells (PEMFC) [80°C, H⁺]
- Direct-Methanol Fuel Cells (DMFC) [80°C, H⁺]
- Alkaline Fuel Cells (AFC) [150°C, OH⁻]
- Phosphoric Acid Fuel Cells (PAFC) [220°C, H⁺]
- Protonic Ceramic Fuel Cell (PCFC) [650°C, H⁺]
- Molten Carbonate Fuel Cells (MCFC) [700°C, CO₃²⁻]
- Solid Oxide Fuel Cells (SOFC) [900°C, O²⁻]
Operating Temperature: A Key Characteristic

- **Low Temperature Fuel Cell Advantages**
  - Quick start-up to operating temperature (~100°C)
  - Wide range of cell construction materials

- **High Temperature Fuel Cell Advantages**
  - Fuel flexibility via internal fuel reforming
  - Inexpensive, base metal electrocatalysts
  - Easier heat recovery for increased efficiency

- **Intermediate Temperature Fuel Cells: The Best of Both Worlds?**
  - Precious metal catalysts not needed above ~300°C
  - Stainless steel internals may be used below ~750°C
Hydrogen Fuel Cells

**Advantages of Hydrogen Fuel**
- Fast electrocatalytic reaction
- Protons \([H^+]\) or hydronium ions \([H_3O^+]\) conduct rapidly across acidic membranes
- Very high energy to weight ratio
- Carbon-free: eliminates local CO\(_2\) pollution

**Disadvantages**
- Compressed H\(_2\): poor energy to volume ratio
- Liquefied H\(_2\): cryogenic; very energy intensive to create and maintain
- Safety for handling and storage a very big concern
On-board vs. Internal Reforming

- **Improved System Efficiency**
  - Higher fuel energy density
  - Easier fuel distribution

- **Fuel Reformers**
  - Thermally isolated or integrated
  - May be bulky, problematic

- **Direct Fuel Cells**
  - Internal reforming of fuel
  - Mostly high temperature FCs
  - Reaction intermediates may require consideration

50 kW natural gas reformer
Harvest Energy Technology
Ammonia as a Fuel Cell Fuel

2 NH\(_3\) → 3 H\(_2\) + N\(_2\) \(\Delta H^\circ = 46 \text{ kJ/mol}\)

- Very mild enthalpy of reforming
- NH\(_3\) is a liquid at room temperature and 10 atm
  - Power density is comparable to other liquid fuels
  - Vaporizes when throttled (no flash line required)
- Essentially non-flammable, non-explosive
- 180 kWh of electricity from 15 gallons ammonia (38 kg) with 50% efficient fuel cell system
- Well-established transport and storage infrastructure already in place
Externally reformed ammonia
- Trace $\text{NH}_3$ incompatible with PEM
- Trace amounts limited by chemical equilibrium
- Reformate usually must be scrubbed

Medium/high temperature fuel cells
- PAFC: Trace $\text{NH}_3$ reacts with acid electrolyte
- MCFC: $\text{NH}_3$ crossover, $\text{CO}_2$ recycling complication
- SOFC: An excellent fuel choice, but some $\text{NO}_x$
- PCFC: An excellent fuel choice, no $\text{NO}_x$
Ammonia Catalysis

- Dual combinations of transition metals used for industrial ammonia processes
  - Ammonia synthesis
  - Ammonia decomposition
  - Ammonia oxidation
- Interesting combinations: Ru/Pd, Fe/Ni
Ammonia Decomposition

Temperature (deg C)

Fractional Am

Ru
Pt
Ir
Fe
Ni
Cu
Cr
Co
Rh
Pd
Ammonia Oxidation

\[ \text{NH}_3 + \frac{3}{4} \text{O}_2 \rightarrow \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2\text{O} \quad \Delta H^o = -382 \text{ kJ/mol} \]

- **Catalytic combustion**
  - Start-up heat source for fuel cells
  - Satisfies “one-fuel” approach

- **Nitrogen oxide control**
  - Oxidation catalysts (Cu, Fe, Cr)
  - Ammonia injection

\[ \text{NO}_x + \text{NH}_3 \rightarrow \text{H}_2\text{O} + \text{N}_2 \]
# Fuel Comparison

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Base MJ / liter</th>
<th>Reformed MJ / liter*</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ (5000 psia)</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>H₂ (liq.)</td>
<td>9.9</td>
<td>9.9</td>
</tr>
<tr>
<td>NH₃ (liq.)</td>
<td>15.3</td>
<td>13.6</td>
</tr>
<tr>
<td>Methanol</td>
<td>17.9</td>
<td>10.2</td>
</tr>
<tr>
<td>Ethanol</td>
<td>23.4</td>
<td>9.1</td>
</tr>
<tr>
<td>Propane (liq.)</td>
<td>29.4</td>
<td>8.6</td>
</tr>
<tr>
<td>Gasoline</td>
<td>36.2</td>
<td>9.2</td>
</tr>
<tr>
<td>JP-8</td>
<td>40.5</td>
<td>9.7</td>
</tr>
</tbody>
</table>

* Includes heat and water volume required for steam reforming
## Direct Fuel Cell Comparison

<table>
<thead>
<tr>
<th>Fuel Utilized (Electrolyte Type)</th>
<th>Direct Ammonia (PCC)</th>
<th>H₂ Gas (PEM)</th>
<th>Hydrocarbon (SOFC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Temperature (°C)</td>
<td>500 - 750</td>
<td>20 - 100</td>
<td>800 - 1000</td>
</tr>
<tr>
<td>Materials Construction Cost</td>
<td>Moderate to low (stainless steel)</td>
<td>Low (aluminum)</td>
<td>High (metal oxides/ceramics)</td>
</tr>
<tr>
<td>Electrocatalyst Cost (Type)</td>
<td>Low (Ni, Co, La, Mn)</td>
<td>High (Pt, Pd, Ru)</td>
<td>Low (Ni, Co, La, Mn)</td>
</tr>
<tr>
<td>Water Product Discharge</td>
<td>At cathode, into air stream</td>
<td>At cathode, into air stream</td>
<td>At anode, dilutes fuel</td>
</tr>
</tbody>
</table>
- Utilizes inexpensive base metal catalyst (Ni or Co)
  - Operating temperature 800-1000°C, depending on electrolyte
  - Elevated temperature allows direct ammonia utilization
- Complete ammonia conversion not possible
- Fuel diluted by steam, product nitrogen
- NO\textsubscript{x} may appear in exhaust
NH$_3$/SOFC Performance

- **Standard SOFC**
  - YSZ electrolyte
  - Ni anode
  - LSM cathode
- **Carbon-free**
  - Dry fuel
  - Faster kinetics
- **Conclusions**
  - High NH$_3$ conversion
  - NOx formed at anode
  - Virtually no difference between NH$_3$ and H$_2$ feeds

N. Dekker, B. Rietveld ECN (2004)
Proton Conducting Perovskites

**General characteristics**
- $\text{ABO}_3$ ($\text{A}^{+2}$, $\text{B}^{+4}$)
- Must be doped with lower-valence (acceptor) elements
- Oxygen vacancies replaced by protons after steam treatment

**Complex perovskites**
- $\text{A}_2(\text{B'}\text{B''})\text{O}_6$ ($\text{A}^{+2}$, $\text{B'}^{+3}$, $\text{B''}^{+5}$)
- Comparable conductivities to simple perovskites
- “Doping” possible by adjustment of $\text{B'}/\text{B''}$ ratio

(AIST, Japan)
Pure Hydrogen from Ammonia Reformate

- **Protonic ceramic applied as a hydrogen pump**
  - Separation of hydrogen from stream impurities
  - Pressurization of hydrogen stream
- **Removal of CO from syngas**
- **Dehydrogenation reactions to produce propylene, ethylene, acetylene**

![Diagram of hydrogen production process](image)
**Protonic Ammonia Electrolyzer**

- **Substitution of thermal energy with electric power**
  - “Cracked” hydrogen stream is nitrogen-free
  - Mild decomposition energy requires little electric power

- **Complete ammonia conversion possible!**

- **If operated with recycle, will require purging to avoid N₂ buildup**
Protonic Ammonia Synthesis

- An alternative to packed-bed heterogeneous catalysis
  - Verified experimentally
  - May also use higher alkenes for hydrogen source
- May be carried out at atmospheric pressure!
- Limited by thermodynamic equilibrium, just as in Haber synthesis
The Protonic Ammonia Fuel Cell

- Utilizes inexpensive base metal catalyst (Ni or Co)
  - Operating temperature 450-700°C, depending on catalyst
  - Elevated temperature increases electrode kinetics
- Complete ammonia conversion IS possible!
- Fuel not diluted by steam
- NO\textsubscript{x}-free exhaust
Questions?