Sustainable Energy
Mod. 1: Fuel Cells & Distributed Generation Systems

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Lesson V: fuel cells (MCFC)
Main Characteristics

- Operate at 650°C.
- Noble metal catalysts are not required.
- Developed for natural gas and coal-based power plants for industrial, electrical utility, and military applications.
- Higher overall system efficiencies.
- Greater flexibility in the use of available fuels.
- Severe problems on the corrosion stability.
- Electrolyte management, that is, control over the optimum distribution of molten carbonate electrolyte in the different cell components, is critical for achieving high performance and endurance with MCFCs.
- Various processes (i.e., consumption by corrosion reactions, potential driven migration, creepage of salt and salt vaporization) need to be mitigated.
Reaction Process (1/3)

Anode side:

\[ \text{H}_2 + \text{CO}_3^{=} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2e^- \]

Cathode side:

\[ \frac{1}{2}\text{O}_2 + \text{CO}_2 + 2e^- \rightarrow \text{CO}_3^{=} \]

Overall reaction:

\[ \text{H}_2 + \frac{1}{2}\text{O}_2 + \text{CO}_2 \text{ (cathode)} \rightarrow \text{H}_2\text{O} + \text{CO}_2 \text{ (anode)} \]

Nernst voltage:

\[ E = E^\circ + \frac{RT}{2F} \ln \frac{P_{\text{H}_2}P_{\text{CO}_2}}{P_{\text{H}_2\text{O}}^2} + \frac{RT}{2F} \ln \frac{P_{\text{CO}_2}}{P_{\text{CO}_2}} \]
The need for CO$_2$ at the cathode requires some schemes:

- transfer the CO$_2$ from the anode exit gas to the cathode inlet gas ("CO$_2$ transfer device")
- produce CO$_2$ by combusting the anode exhaust gas, which is mixed directly with the cathode inlet gas
- supply CO$_2$ from an alternate source.

It is usual practice in an MCFC system that the CO$_2$ generated at the anode (right side of Equation) be routed (external to the cell) to the cathode (left side of Equation).
Reaction Process (3/3)

Porous Ni anode
Porous NiO cathode

\[ \text{Molten Carbonate/LiAlO}_2 \text{ electrolyte structure} \]

\[ \text{Fuel gas} \]
\[ \text{Oxidant gas} \]

\[ \text{H}_2 + \text{CO}_3^{\text{aq}} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{CO}_3^{\text{aq}} \]

\[ \frac{1}{2}\text{O}_2 + \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{\text{aq}} \]
### Cell Components (history) (1/2)

<table>
<thead>
<tr>
<th>Component</th>
<th>Ca. 1965</th>
<th>Ca. 1975</th>
<th>Current Status</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anode</strong></td>
<td>Pt, Pd, or Ni</td>
<td>Ni-10 Cr</td>
<td>Ni-Cr/Ni-Al/Ni-Al-Cr, 3-6 μm pore size, 45 to 70 percent initial porosity, 0.20 to 0.5 mm thickness, 0.1 to 1 m²/g</td>
</tr>
<tr>
<td><strong>Cathode</strong></td>
<td>Ag₂O or lithiated NiO</td>
<td>lithiated NiO</td>
<td>lithiated NiO-MgO, 7 to 15 μm pore size, 70 to 80 percent initial porosity, 0.5 to 1 mm thickness, 0.5 m²/g</td>
</tr>
<tr>
<td><strong>Electrolyte Support</strong></td>
<td>MgO</td>
<td>mixture of α-, β-, and γ-LiAlO₂</td>
<td>γ-LiAlO₂, α-LiAlO₂, 0.5 to 12 m²/g, 0.2 to 1 mm thickness</td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td>52 Li-48 Na, 43.5 Li-31.5 Na-25 K</td>
<td>62 Li-38 K</td>
<td>62 Li-38 K, 60 Li-40 Na, 51 Li-48 Na, tape cast, 0.5 to 1 mm thickness</td>
</tr>
<tr>
<td>* (wt percent)</td>
<td>&quot;paste&quot;</td>
<td>hot press &quot;tile&quot;</td>
<td></td>
</tr>
</tbody>
</table>
The conventional process to fabricate electrolyte structures until about 1980 involved hot pressing mixtures of LiAlO$_2$ and alkali carbonates. These electrolyte structures were relatively thick (1 to 2 mm) and difficult to produce in large sizes because large tooling and presses were required. To overcome these problems, alternative processes were developed: tape casting and electrophoretic deposition (thin electrolyte structures).
Electrolyte Fabrication Process

- The tape casting and electrophoretic deposition processes are able to produce electrolyte structures of 0.25-0.5 mm (thickness is linked with ohmic losses).

\[ \Delta V_{\text{ohm}} (V) = 0.5t \]

- Higher ionic conductivities, and hence lower ohmic polarization, are achieved with Li-rich electrolytes because of the relative high ionic conductivity of Li$_2$CO$_3$ compared to that of Na$_2$CO$_3$ and K$_2$CO$_3$. However, gas solubility and diffusivity are lower, and corrosion is more rapid in Li$_2$CO$_3$.
- NiO dissolution problems for Ni-based anodes.
- The CO$_2$ partial pressure is an important parameter in the dissolution of NiO in carbonate melts because the basicity is directly proportional to log PCO$_2$. An MCFC usually operates with a molten carbonate electrolyte that is acidic.
Anode

- State-of-the-art anodes are made of a Ni-Cr/Ni-Al alloy.
- However, Ni-Cr anodes are susceptible to creep when placed under the torque load required in the stack to minimize contact resistance between components.
- Developers are trying lesser amounts of Cr (creep increase).
- Other developers have tested Ni-Al alloy anodes.
- Alloys, such as Cu-Al and LiFeO₂, have not demonstrated sufficient creep strength or performance.
- Tests are being conducted on ceramic anodes to alleviate the problems related to sulphur poisoning, being experienced with anodes.
- At the present time, no alternative anodes have been identified for avoiding sulphur poisoning.
Cathode

✔ State-of-the-art cathodes are made of lithiated NiO that have acceptable conductivity and structural strength.
✔ Dissolution of the cathode (nickel) has turned out to be the primary life-limiting constraint of MCFCs.
✔ Developers are investigating approaches (increasing the basicity of the electrolyte with Li/Na₂CO₃) to resolve the NiO dissolution issue.
✔ Tests with LiFeO₂ cathodes showed no dissolution but low performance (further tests with Co-doped LiFeO₂).
✔ Using additives in the electrolyte to increase its basicity:

<table>
<thead>
<tr>
<th></th>
<th>62 MOL percent Li₂CO₃/K₂CO₃</th>
<th>52 MOL percent Li₂CO₃/Na₂CO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>0 to 15</td>
<td>0 to 5</td>
</tr>
<tr>
<td>SrCO₃</td>
<td>0 to 5</td>
<td>0 to 5</td>
</tr>
<tr>
<td>BaCO₃</td>
<td>0 to 10</td>
<td>0 to 5</td>
</tr>
</tbody>
</table>

✔ Another approach is to increase the fraction of Li in the electrolyte or change the electrolyte to Li/Na
Electrolyte Matrix

- Structure materials are tightly packed, fine \( \alpha \)- or \( \gamma \)-LiAlO\(_2\) with fibber or particulate reinforcement.
- The matrix must also be strong enough to counter operating mechanical and thermal stresses, and still maintain the gas seal.
- Ceramic fibber reinforcement is most effective for crack deflection, followed by platelet and sphere forms.
- The industry trend is to switch from \( \gamma \)-LiAlO\(_2\) to \( \alpha \)-LiAlO\(_2\) for better long-term phase and particle-size stabilities.
- Studies for cost reduction.
Electrolyte

✓ Present electrolytes have the following chemistry: lithium potassium carbonate, Li₂CO₃/K₂CO₃ (62:38 mol percent) for atmospheric pressure operation and lithium sodium carbonate, LiCO₃/NaCO₃ (52:48 or 60:40 mol percent) that is better for improved cathode stability under pressurized operation and life extension.
✓ Evaporation of the electrolyte is a life-limiting issue for the molten carbonate fuel cell.
✓ Thicker electrolytes result in a longer time to shorting by internal precipitation.
✓ Li/Na also provides better corrosion resistance to mitigate acidic cathode dissolution.
✓ Another area for electrolyte improvement is the ability to prevent gas crossover.
Bipolar Plate

✓ Present bipolar plate consists of a separator, current collectors, and the wet seal.
✓ The separator and current collector is Ni-coated 310S/316L.
✓ The wet seal is formed by aluminization of the metal.
✓ Low oxygen partial pressure on the anode side of the bipolar plate prevents the formation of a protective oxide coating. After reaction with the thin, creeping electrolyte, heat-resistant alloys form a multi-layered corrosion scale.
✓ More expensive nickel-based alloys resist corrosion as well as or only slightly better than austenitic stainless steels.
Performance

✓ Typical MCFCs will generally operate in the range of 100 to 200 mA/cm$^2$ at 750 to 900 mV/cell.
✓ Cathodic side composition (effect of dilution with inert gas):
  ✓ Curve 1: 12.6% O$_2$/18.4% CO$_2$/69.0% N$_2$
  ✓ Curve 2: 33% O$_2$/67% CO$_2$ (no N$_2$)
# Parameter Change Influence

✓ Empirical equations for changes (1->2) in pressure, temperature and....

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
<th>Comments</th>
</tr>
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<tbody>
<tr>
<td>Pressure</td>
<td>$\Delta V_p (mV) = 78.5 \log \frac{P_2}{P_1}$</td>
<td>$1 \ atm \leq P \leq 10 \ atm$</td>
</tr>
<tr>
<td>Temperature</td>
<td>$\Delta V_T (mV) = 2.16 \left( \frac{T_2}{T_1} - 1 \right)$</td>
<td>$575^\circ C \leq T &lt; 600 \ ^\circ C$</td>
</tr>
<tr>
<td></td>
<td>$\Delta V_T (mV) = 1.40 \left( \frac{T_2}{T_1} - 1 \right)$</td>
<td>$600^\circ C \leq T &lt; 650 \ ^\circ C$</td>
</tr>
<tr>
<td></td>
<td>$\Delta V_T (mV) = 0.25 \left( T_2 - T_1 \right)$</td>
<td>$650^\circ C &lt; T \leq 700 \ ^\circ C$</td>
</tr>
<tr>
<td>Oxidant</td>
<td>$\Delta V_{cathode} (mV) = 250 \log \frac{P_{CO_2}^{1/2} P_{O_2}}{P_{CO_2}^{1/2} P_{O_2}^{1/2}}$</td>
<td>$0.04 \leq \frac{P_{CO_2}}{P_{O_2}} \leq 0.11$</td>
</tr>
<tr>
<td></td>
<td>$\Delta V_{cathode} (mV) = 99 \log \frac{P_{CO_2}^{1/2} P_{O_2}}{P_{CO_2}^{1/2} P_{O_2}^{1/2}}$</td>
<td>$0.11 \leq \frac{P_{CO_2}}{P_{O_2}} \leq 0.38$</td>
</tr>
<tr>
<td>Fuel</td>
<td>$\Delta V_{anode} (mV) = 173 \log \frac{(P_{H_2} / P_{CO_2})^{1/2} (P_{H_2O} / P_{CO_2})^{1/2}}{(P_{H_2} / P_{CO_2})^{1/2} (P_{H_2O} / P_{CO_2})^{1/2}}$</td>
<td>$50 \leq J \leq 150 \text{ mA/cm}^2$</td>
</tr>
<tr>
<td></td>
<td>$\Delta V_J (mV) = -1.21 \Delta J$</td>
<td>$150 &lt; J \leq 200 \text{ mA/cm}^2$</td>
</tr>
<tr>
<td>Density</td>
<td>$\Delta V_J (mV) = -1.76 \Delta J$</td>
<td></td>
</tr>
<tr>
<td>Life Effects</td>
<td>$\Delta V_{lifetime} (mV) = -5 \text{ mV/1000 hours}$</td>
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</table>
In a conventional fuel cell system, fuel is processed in a **reformer** where it is steam reformed to produce \( \text{H}_2 \) (and other products: \( \text{CO}, \text{CO}_2 \)).

In high-temperature fuel cells where the steam reforming reaction can be sustained with catalysts: **internal reformer**.

The internal reforming MCFC eliminates the need for the external fuel processor (high efficient, simple, reliable, and cost effective system).

Two alternate approaches to internal reforming molten carbonate cells:

- **indirect internal reforming (IIR)**
- **direct internal reforming (DIR)**

Methane is a common fuel in internal reforming MCFCs:

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2
\]

Steam reforming reaction is **endothermic**, with \( \Delta H \) = 53.87 kcal/mol.

A supported Ni catalyst (e.g., Ni supported on MgO or LiAlO\(_2\)) sustains the steam reforming reaction at 650 °C to produce sufficient \( \text{H}_2 \).
Internal Reforming (2/3)
Internal Reforming (3/3)

✓ Interrelationship between the conversion of CH4 to H2 and its utilization in an internal reforming MCFC at 650 °C