Fuel Cell Operation

- electrochemical energy conversion device
- nonconsumable anode and cathode
- oxidation-reduction reaction converted directly into electrical energy without a intermediary conversion into heat — more efficient than the Carnot cycle — as high as 90% efficiency theoretically possible
- reactants (typically gaseous) external to energy conversion device
- electrolyte layer in contact with a porous anode and cathode, provides reactant and ionic transport as well as physical barrier to separate fuel and oxidant
- ionic transport can be positive or negative

Fuel Cell Classification

<table>
<thead>
<tr>
<th>PEMFC</th>
<th>AFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>electrolyte</td>
<td>ion exchange membrane</td>
<td>KOH in asbestos matrix</td>
<td>phosphoric acid in silicon carbide</td>
<td>alkali carbonates in LiAlO2 matrix</td>
</tr>
<tr>
<td>charge carrier</td>
<td>H⁺</td>
<td>OH⁻</td>
<td>H⁺</td>
<td>CO₃⁻</td>
</tr>
<tr>
<td>operating temperature</td>
<td>~ 80°C</td>
<td>~ 130°C</td>
<td>~ 900°C</td>
<td>~ 650°C</td>
</tr>
<tr>
<td>catalyst</td>
<td>platinum</td>
<td>various</td>
<td>platinum</td>
<td>nickel</td>
</tr>
<tr>
<td>product water management</td>
<td>evaporative (hopefully)</td>
<td>evaporative</td>
<td>evaporative</td>
<td>gaseous product</td>
</tr>
<tr>
<td>product heat management</td>
<td>process gas &amp; cooling system</td>
<td>process gas &amp; cooling system</td>
<td>internal reforming &amp; process gas</td>
<td>internal reforming &amp; process gas</td>
</tr>
<tr>
<td>fuel</td>
<td>pure H₂, tolerates CO₂</td>
<td>pure H₂, tolerates CO₂, ~1% CO</td>
<td>pure H₂, tolerates CO₂</td>
<td>H₂, CO, CH₄, other hydrocarbons</td>
</tr>
</tbody>
</table>

© Also known as solid polymer fuel cell (SPFC)
PEM Fuel Cell Kinetics

O₂ reduction half reaction - cathode
\[ \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O + \text{heat} \]

H₂ oxidation half reaction - anode
\[ H_2 + 2H^+ + 2e^- \rightarrow 2H_2O \]

Overall cell reaction
\[ \frac{1}{2}O_2 + H_2 \rightarrow H_2O + \text{heat} \]

performance limited by rate of O₂ reduction which is more than 100 times slower than the H₂ oxidation

Polarization Losses

Theoretical EMF or ideal voltage

Activation Polarization (reaction rate loss)

Ohmic Polarization (resistance loss)

Concentration Polarization (gas transport loss)

Activation Polarization losses due to oxidation/reduction kinetics
Ohmic Polarization losses due to resistance in electron and ionic conduction
Concentration Polarization excess water "floods" the gas diffusion layer or "plugs" the gas flow channel

water management is critical to the performance of a PEM fuel cell
Electrochemical Reactions

<table>
<thead>
<tr>
<th>Common Fuels</th>
<th>Acid Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>Anode half reaction: $2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^-$</td>
</tr>
<tr>
<td>CH₄</td>
<td>Cathode half reaction: $0\text{₂} + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>$2\text{H}_2 + 0\text{₂} \rightarrow 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>C</td>
<td>Alkaline Electrolyte</td>
</tr>
<tr>
<td>CH₂O₂</td>
<td>Anode half reaction: $2\text{H}_2 + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O} + 4\text{e}^-$</td>
</tr>
<tr>
<td>NH₃</td>
<td>Cathode half reaction: $0\text{₂} + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$</td>
</tr>
<tr>
<td>N₂H₄</td>
<td>$2\text{H}_2 + 0\text{₂} \rightarrow 2\text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>

Energy Available for Conversion

The total energy change of the reactants is the difference in enthalpy of formation.

$$\Delta H_f = \sum \Delta H_f^{products} - \sum \Delta H_f^{reactants}$$

$$\Delta H_f > 0 \quad \text{exothermic}$$

$$\Delta H_f < 0 \quad \text{endothermic}$$

Apply 1st Law of Energy to the Control Volume

$$\dot{Q}_{out} - \dot{W}_e = \Delta E = \Delta H$$

No changes in kinetic or gravitational potential energies

The maximum work (power) will occur if the thermal power portion of the enthalpy change is reversible.

$$\Delta Q_{rev} = T \Delta S$$

Fuel cells typically operate isothermally, therefore,

$$\dot{Q}_{out} = T \Delta S$$

$$-\dot{W}_e \leq \Delta H - T \Delta S$$

$$-\dot{W}_e \leq \sum \Delta G^{products} - \sum \Delta G^{reactants}$$

$$\Delta G_{r,p} = \Delta G - T \Delta S \leq 0$$

criteria for a spontaneous reaction:
Gaseous Reactants

- Treating the reactants as an ideal gas, \( P_Y = \frac{nR}{T} \).
- For an ideal gas: \( TdS = dh - n \Delta P \) (Gibbs equation)

\[
\begin{align*}
&\quad dG = dh - TdS = \Delta dP \\
&\quad dG = nRT \frac{\Delta P}{P}
\end{align*}
\]
- For an isothermal process:

\[
G_2 - G_1 = nRT \ln \left( \frac{P_2}{P_1} \right)
\]

- Tabulated values of Gibbs Free Energy (and enthalpy of formation) are given relative to a reference state.

\[
G = G^0 + nRT \ln \left( \frac{P}{P_0} \right)
\]

Reference state typically at \( P_0 = \text{atm} \) (but NOT ALWAYS!)

\[
\frac{P}{P_0} \text{ is also known as activity}
\]

Electrical Work

\[
W_e = neFE
\]

\( E \) is voltage difference across electrodes

Faraday's constant = 96,487 C/mol-elect

1 mol of electron per mol of fuel

The change in Gibbs Free Energy at reference state is \( \Delta G^0 = -neFE \)

Thus, \( E^0 = \frac{-\Delta G^0}{neF} \)

Maximum Conversion Efficiencies

Heat Engine: \( \eta_{\text{th}} = 1 - \frac{T_{\text{low}}}{T_{\text{high}}} \)

Fuel Cell: \( \eta_{\text{th}} = \frac{W_e}{\Delta V} = \frac{\Delta G}{\Delta H} = \frac{neFE}{\Delta H} \)

\( \eta_{\text{th max}} = \frac{neFE^0}{\Delta H} \); For \( \text{H}_2 - \text{O}_2 \) reaction at 25°C and 1 atm, \( E^0 = 1.23 \text{ V.} \)
3.6.3. Thermodynamic Efficiency

For the case of an electrochemical energy converter working ideally, it has been shown that the free-energy change of the reaction may be totally converted to electrical energy. Thus, an electrochemical energy converter has a thermodynamic efficiency given by:

\[
\eta_{th} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H}
\]  

(3.65)

Table 3-1. Thermodynamic Data for some Candidate Fuel-Cell Reactions Under Standard Conditions at 25 °C.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Reaction</th>
<th>n</th>
<th>(-\Delta H^0) [kJ/mol]</th>
<th>(-\Delta G^0) [kJ/mol]</th>
<th>(E^0) rev. [V]</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>(H_2 + 0.5 \text{ O}_2 \rightarrow \text{H}_2\text{O}_2)</td>
<td>2</td>
<td>286.0</td>
<td>237.3</td>
<td>1.229</td>
<td>83.0</td>
</tr>
<tr>
<td></td>
<td>(H_2 + \text{Cl}<em>2 \rightarrow 2 \text{HCl}</em>{(\text{aq})})</td>
<td>2</td>
<td>335.5</td>
<td>262.5</td>
<td>1.359</td>
<td>78.3</td>
</tr>
<tr>
<td></td>
<td>(H_2 + \text{Br}_2 \rightarrow 2 \text{HBr})</td>
<td>2</td>
<td>242.0</td>
<td>205.7</td>
<td>1.066</td>
<td>85.0</td>
</tr>
<tr>
<td>Methane</td>
<td>(\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}_2)</td>
<td>8</td>
<td>890.8</td>
<td>818.4</td>
<td>1.060</td>
<td>91.9</td>
</tr>
<tr>
<td>Propane</td>
<td>(\text{C}_3\text{H}_8 + 5 \text{O}_2 \rightarrow 3 \text{CO}_2 + 4 \text{H}_2\text{O}_2)</td>
<td>20</td>
<td>2221.1</td>
<td>2109.9</td>
<td>1.093</td>
<td>95.0</td>
</tr>
<tr>
<td>Decane</td>
<td>(\text{C}<em>{10}\text{H}</em>{22} + 15.5 \text{O}_2 \rightarrow 10 \text{CO}_2 + 11 \text{H}_2\text{O}_2)</td>
<td>66</td>
<td>6832.9</td>
<td>6590.5</td>
<td>1.102</td>
<td>96.5</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>(\text{CO} + 1.5 \text{O}_2 \rightarrow \text{CO}_2)</td>
<td>2</td>
<td>283.1</td>
<td>257.2</td>
<td>1.066</td>
<td>90.9</td>
</tr>
<tr>
<td>Carbon</td>
<td>(\text{C} + 0.5 \text{O}_2 \rightarrow \text{CO})</td>
<td>2</td>
<td>110.6</td>
<td>137.3</td>
<td>0.712</td>
<td>124.2</td>
</tr>
<tr>
<td></td>
<td>(\text{C} + \text{O}_2 \rightarrow \text{CO}_2)</td>
<td>4</td>
<td>393.7</td>
<td>394.6</td>
<td>1.020</td>
<td>100.2</td>
</tr>
<tr>
<td>Methanol</td>
<td>(\text{CH}_3\text{OH} + 1.5 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}_2)</td>
<td>6</td>
<td>726.6</td>
<td>702.5</td>
<td>1.214</td>
<td>96.7</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>(\text{CH}<em>2\text{O}</em>{(g)} + \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}_2)</td>
<td>4</td>
<td>561.3</td>
<td>522.0</td>
<td>1.350</td>
<td>93.0</td>
</tr>
<tr>
<td>Formic-acid</td>
<td>(\text{HCOOH} + 0.5 \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}_2)</td>
<td>2</td>
<td>270.3</td>
<td>285.5</td>
<td>1.480</td>
<td>105.6</td>
</tr>
<tr>
<td>Ammonia</td>
<td>(\text{NH}_3 + 0.75 \text{O}_2 \rightarrow 0.5 \text{N}_2 + 1.5 \text{H}_2\text{O})</td>
<td>3</td>
<td>382.8</td>
<td>338.2</td>
<td>1.170</td>
<td>88.4</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>(\text{N}_2\text{H}_4 + \text{O}_2 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O}_2)</td>
<td>4</td>
<td>622.4</td>
<td>602.4</td>
<td>1.560</td>
<td>96.8</td>
</tr>
</tbody>
</table>
Finding \( \Delta G \)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Heat of Formation ( h_f^\circ ) [kJ/mol]</th>
<th>Gibbs Free Energy ( \Delta G^\circ ) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen gas ( \text{H}_2 )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Oxygen gas ( \text{O}_2 )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Water vapor ( \text{H}_2\text{O}(g) )</td>
<td>-241820</td>
<td>-228590</td>
</tr>
<tr>
<td>Liquid water ( \text{H}_2\text{O}(l) )</td>
<td>-285830</td>
<td>-237180</td>
</tr>
<tr>
<td>Carbon monoxide ( \text{CO} )</td>
<td>-110530</td>
<td>-137150</td>
</tr>
<tr>
<td>Carbon dioxide ( \text{CO}_2 )</td>
<td>-393520</td>
<td>-313360</td>
</tr>
</tbody>
</table>

(from Sergey I. Bolea, Table A-22)

On a molar basis, \( \Delta G = \Delta G^\circ - RT \ln \left( \frac{P}{P_0} \right) \); \( P_0 \) is the reference state pressure, which is typically 1 atm.

- For a generic chemical reaction:
  \[ \alpha A + b B \rightarrow \mu M + n N \]

  where \( A \) is the fuel and \( a, b, \mu, \) and \( n \) are the stoichiometric coefficients.

  \[ \Delta G = \left( m \overline{\Delta G}_m - n \overline{\Delta G}_N \right) - \left( a \overline{\Delta G}_A - b \overline{\Delta G}_B \right) \]

  products  reactants

- On a per mol of fuel basis,

  \[ \Delta G = \left( \frac{\mu}{a} \right) \overline{\Delta G}_m + \left( \frac{n}{a} \right) \overline{\Delta G}_N - \overline{\Delta G}_A - \left( \frac{b}{a} \right) \overline{\Delta G}_B \]

  \[ = \left( \frac{\mu}{a} \right) \overline{\Delta G}_m + \left( \frac{n}{a} \right) \overline{\Delta G}_N - \left( \frac{b}{a} \right) \overline{\Delta G}_B \]

  \[ + \frac{\ln \left( \frac{P\alpha}{P_0} \right)}{\Delta G^\circ} \] (known as the reaction coefficient, \( K \))

  \[ \Delta G = \Delta G^\circ - RT \ln K \]

- When the reference pressure is 1 atm, and reactant/product pressures are expressed in atm, and when the stoichiometric coefficient for the fuel is 1 mol (\( a = 1 \)), then the change in Gibbs free energy is commonly written as:

  \[ \Delta G = \Delta G^\circ + RT \ln \left( \frac{P_a P_b}{P_m P_n} \right) \]

  - Note the sign change.
FIGURE 3.10 The reversible work produced by a H₂/O₂ fuel cell is greater than that of a Carnot engine at temperatures below 950 K. At higher temperatures, the Carnot engine is able to convert more of the HHV of H₂ (285.840 kJ/mol) into work. The data for the standard Gibbs energy of formation for water vapor was taken from Lide (1995, pp. 5–64).
At non-standard state,

\[ E = E^0 + \frac{RT}{nF} \ln \left( \frac{\text{Reactants}}{\text{Products}} \right) \]

Nernst Equation
Determine the heating value of \( \text{H}_2 \) at 300 °C. Reactants and oxidants are at 1 atm.

\( \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \)

At 300 °C and 1 atm, this will be in vapor form.

\[
\Delta h^\circ = \sum_{\text{products}} \overline{h}^\circ - \sum_{\text{reactants}} \overline{h}^\circ
\]

\[
\Delta h^\circ = \left[ \left( \frac{1 \text{ mol H}_2}{\text{kcal}} \right) \left( 2858.30 \frac{\text{kJ}}{\text{kcal}} \right) \right] - \left[ \left( \frac{1 \text{ mol H}_2}{\text{kcal}} \right) (0) + \left( \frac{1 \text{ mol O}_2}{2 \text{ kcal}} \right) (0) \right]
\]

\[
\Delta h^\circ = -2858.30 \frac{\text{kJ}}{\text{kcal}} = -\frac{\text{HHV of H}_2}{\text{product}} = -(\text{HHV} + h^\circ_{\text{H}_2\text{O}}) - h^\circ_{\text{vaporization}}
\]

\[
\Delta h_{\text{vap}} = \Delta h^\circ - h^\circ_{\text{H}_2\text{O}}(300^\circ \text{C}) = -241820 \frac{\text{kJ}}{\text{kcal}}
\]
Determine the maximum conversion efficiency and open circuit voltage for a hydrogen-oxygen (in air) fuel cell operating at (a) 75°C and (b) 300°C. The products exhaust to 1 atm, the hydrogen is supplied at 2 atm, and the oxygen is supplied (in air) at 1.5 atm.

(a) At 75°C — product water is in liquid form

\[ \Delta h_f^o = -285830 \frac{kJ}{kmol H_2} \]

\[ \Delta \bar{g}^o = \left( \frac{kmol H_2}{kmol Hz} \right) \left( -327150 \frac{kJ}{kmol Hz O_2 Hz} \right) \left( \frac{1}{2} (0) + \left( \frac{1}{2} \right) (0) \right) = -327150 \frac{kJ}{kmol Hz} \]

\[ \Delta \bar{g}_{75^\circ C} = \Delta \bar{g}^o + RT \ln \left( \frac{P_{H_2}}{P_{O_2}} \right) = \left( -327150 \frac{kJ}{kmol Hz} \right) + \left( 8.34 \frac{kJ}{kmol Hz} \right) \ln \left( \frac{1}{1.5 \times 0.21} \right) = 0.1156 \]

\[ \Delta \bar{g}_{75^\circ C} = -236846 \frac{kJ}{kmol Hz} \]

(b) at 300°C — product water is in vapor form

\[ \Delta h_f^o = -241820 \frac{kJ}{kmol Hz} \]

\[ \Delta \bar{g}^o = -228590 \frac{kJ}{kmol Hz} \]

\[ \Delta \bar{g}_{300^\circ C} = \Delta \bar{g}^o + RT \ln \left( \frac{2 \times (1.5 \times 0.21)^{0.5}}{1} \right) = -228040 \frac{kJ}{kmol Hz} \]

**Maximum Conversion Efficiency**

(a) \[ \eta = \frac{\Delta \bar{g}^o}{\Delta h_f^o} = \frac{-236846 \frac{kJ}{kmol Hz}}{-285830 \frac{kJ}{kmol Hz}} = 0.829 \]

(b) \[ \eta = \frac{-228040 \frac{kJ}{kmol Hz}}{-285830 \frac{kJ}{kmol Hz}} = 0.799 \]

For fuel cells, the higher heating value is used even when the product water is in vapor form.

**Open Circuit Voltage**

\[ E = E^o - RT \ln (K) \]

(a) \[ E_{75^\circ C} = 1.227 V \]

(b) \[ E_{300^\circ C} = 1.18 V \]

\[ \eta = \frac{2 \text{ kmol Hz}}{\text{ kmol Hz}} \]


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

Determine the cell voltage and efficiency for CO reacting in air.

\[ E = E^\circ - \frac{RT}{nF} \ln \left( \frac{P_{\text{O}_2}}{P_{\text{CO}_2}} \right) \]

\[ E^\circ = \frac{\Delta G^\circ}{nF} \]

\[ \Delta G^\circ = 1 \frac{\Delta F}{\text{CO}_2} - \Delta G^\circ_{\text{CO}} - 0.5 \Delta G^\circ_{\text{O}_2} = \left( -393.5 \text{ kJ/mol} \right) - \left( -137.1 \text{ kJ/mol} \right) \times \frac{1}{2} \]

\[ = 1.33 \text{ V} \quad \text{(open circuit potential)} \]

\[ E = E^\circ - \frac{RT}{nF} \ln \left( \frac{P_{\text{O}_2}}{P_{\text{CO}_2}} \right) = 1.33 \text{ V} - \frac{8134 \text{ kJ/mol}}{2 \text{ kJ/mol}} \times \frac{\text{C}^{\circ -}}{2 \text{ kJ/mol}} \ln \left( \frac{1}{1.9 \times 10 \times (0.4485 \times 0.4485)} \right) \]

\[ = 1.33 \text{ V} - (0.0253 \times 0.4485) \]

\[ E = 1.317 \text{ V} \quad \text{(open circuit potential)} \]

\[ \Delta G = -nFE = -25440 \text{ kJ/mol} \]

\[ \Delta H^\circ = -282980 \text{ kJ/mol} \]

\[ \frac{\Delta G}{\Delta H^\circ} = 0.8993 \]