Air Independent Propulsion

For non-nuclear submarines, submersibles and unmanned vehicles; AUV, UUV, torpedoes
Torpedo propulsion was originally stored high pressure air.** It evolved to heated air at the turn of the century using kerosene, alcohol or Otto fuel. Current torpedoes employ electrical storage or lithium sulphur hexafluoride systems. (Sulphur hexafluoride gas is sprayed over a block of lithium which generates heat.

As is well known typical submarine propulsion uses a storage battery with engine recharging. In all the stored systems, the challenge is storage of the oxygen component,

** The initiative behind the self-propelled torpedo was provided by an Austrian frigate captain Giovanni Luppi. After some unsuccessful attempts to propel a charge laden boat with a spring-driven clockwork. In 1864 he turned to Robert Whitehead (1823-1905), then technical manager in an Italian factory to design an improved version. The result was a torpedo in October 1886: length 3.35 m, diameter 25.5 cm, weight 136 kg. Propulsion was provided by 20 to 25 kg of compressed air, driving a reciprocating engine with a high and low pressure cylinder. Taken from "Swedish Torpedo 100 Years; 1876 - 1976.

Secondary Batteries

Lead acid-

\[
Pb + PbO_2 + 2H_2O\rightarrow 2Pt + 4H^+ + 2O_2 \quad \text{energy density 67 lbf/kW*hr}
\]

<table>
<thead>
<tr>
<th>solid</th>
<th>solid</th>
<th>liquid</th>
<th>=</th>
<th>solid</th>
<th>liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>Pb</td>
<td>O_2</td>
<td></td>
<td>2Pt</td>
<td>H_2O</td>
</tr>
<tr>
<td>(2 + 8)·O</td>
<td>2·S</td>
<td>=</td>
<td>(8 + 2)·O</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
2H = 4·H
\]

Silver - Zinc

discharges 1.1 - 0.8 V per cell
charges 1.6 - 2.0 V per cell
electrolyte KOH
energy density 20 lbf/kW*hr

\[
\begin{align*}
\text{discharges} & \quad \text{lbf}\text{}/\text{kW·hr} = 9.072 \text{ kgf}/\text{kW·hr} \\
\text{charges} & \quad \text{lbf}\text{}/\text{kW·hr} = 50 \text{ Wh}/\text{lbf}
\end{align*}
\]

problem (both cells): hydrogen release in charging. New developments: NiCd, Li rechargeable

Fuel Cell

originally developed by Roger Bacon. H_2 and O_2 are supplied to special electrodes with various electrolytes. KOH in the alkaline cells, proton exchange membranes (PEM) and high temperature carbonate in the molten carbonate cells, solid oxides in other cells. Energy conversion is relatively high ~ 60%

\[
H_2 + \frac{1}{2}O_2 = H_2O
\]

complete

\[
H_2 + 2\cdot O\cdot H = 2\cdot H_2O + 2\text{electrons}
\]

\[
\frac{1}{2}O_2 + H_2O = 2\text{electrons} + 2\cdot O\cdot H
\]

theoretical voltage: 1.23 V, practical voltage ~ 0.8 V
maximum power at constant $T_1$

$$\frac{w_{\text{dot}}_{\text{max}}}{m_{\text{dot}}} = h_1 - T_1 s_1 - (h_2 - T_1 s_2) = G_1 - G_2 = \Delta G$$

$G = \text{Gibbs function}$

$h_1 - h_2 = \text{heating value of fuel}$

$$\frac{\Delta G}{\text{hhv}} = 0.825 \text{ to } 0.95$$

depending on $T_1$ and state of $H_2O$ liquid or vapor with internal losses (~ 60% conversion)

$H_2$ consumption:

$$0.111 \text{ lbf/kW-hr} = 0.05 \text{ kgf/kW-hr}$$

$O_2$ consumption:

$$0.889 \text{ lbf/kW-hr} = 0.403 \text{ kgf/kW-hr}$$

reactants

$$1.0 \text{ lbf/kW-hr} = 0.454 \text{ kgf/kW-hr}$$

the volume is important and depends on the storage method: as cryogenic liquids:

$$O_2 \text{ sp.gr} = 1.14 \quad 71 \frac{\text{ lbf}}{\text{ ft}^3} = 1.137 \times 10^3 \frac{\text{ kgf}}{\text{ m}^3}$$

$$H_2 \text{ sp.gr} = 0.064 \quad 4.0 \frac{\text{ lbf}}{\text{ ft}^3} = 64.074 \frac{\text{ kgf}}{\text{ m}^3}$$

A brief description of various electrolyte cells of interest follows. A detailed description of these fuel cells may be found in Sections 3 through 7.

**Polymer Electrolyte Fuel Cell (PEFC):** The electrolyte in this fuel cell is an ion exchange membrane (fluorinated sulfonic acid polymer or other similar polymer) that is an excellent proton conductor. The only liquid in this fuel cell is water; thus, corrosion problems are minimal. Water management in the membrane is critical for efficient performance; the fuel cell must operate under conditions where the byproduct water does not evaporate faster than it is produced because the membrane must be hydrated. Because of the limitation on the operating temperature imposed by the polymer, usually less than 120°C, and because of problems with water balance, a H2-rich fuel is used. Higher catalyst loading (Pt in most cases) than that used in PAFCs is required for both the anode and cathode. Because CO "poisons" the catalyst, the fuel may contain no CO.

**Alkaline Fuel Cell (AFC):** The electrolyte in this fuel cell is concentrated (85 wt%) KOH in fuel cells operated at high temperature (~250°C), or less concentrated (35-50 wt%) KOH for lower temperature (<120°C) operation. The electrolyte is retained in a matrix (usually asbestos), and a wide range of electrocatalysts can be used (e.g., Ni, Ag, metal oxides, spinels, and noble metals). The fuel supply is limited to non-reactive constituents except for hydrogen. CO is a poison, and CO2 will react with the KOH to form K2CO3, thus altering the electrolyte. Even the small amount of CO2 in air is detrimental to the alkaline cell.

**Phosphoric Acid Fuel Cell (PAFC):** Phosphoric acid concentrated to 100% is used for the electrolyte in this fuel cell, which operates at 150 to 220°C. At lower temperatures, phosphoric acid is a poor ionic conductor, and CO poisoning of the Pt electrocatalyst in the anode becomes severe. The relative stability of concentrated phosphoric acid is high compared to other common acids; consequently the PAFC is capable of operating at the high end of the acid temperature range (100 to 220°C). In addition, the use of concentrated acid (100%) minimizes the water vapor pressure so water management in the cell is not difficult. The matrix universally used to retain the acid is silicon carbide (1), and the electrocatalyst in both the anode and cathode is Pt.

**Molten Carbonate Fuel Cell (MCFC):** The electrolyte in this fuel cell is usually a combination of alkali carbonates, which is retained in a ceramic matrix of LiAlO2. The fuel cell operates at 600 to 700°C where the alkali carbonates form a highly conductive molten salt, with carbonate ions providing ionic conduction. At the high operating temperatures in MCFCs, Ni (anode) and nickel oxide (cathode) are adequate to promote reaction. Noble metals are not required.

**Solid Oxide Fuel Cell (SOFC):** The electrolyte in this fuel cell is a solid, nonporous metal oxide, usually Y2O3-stabilized ZrO2. The cell operates at 600-1000°C where ionic conduction by oxygen ions takes place. Typically, the anode is Co-ZrO2 or Ni-ZrO2 cermet, and the cathode is Sr-doped LaMnO3.
### Table 1-1 Summary of Major Differences of the Fuel Cell Types

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>PEFC</th>
<th>AFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ion Exchange Membranes</td>
<td>Mobilized or Immobilized Potassium Hydroxide</td>
<td>Immobilized Liquid Phosphoric Acid</td>
<td>Immobilized Liquid Molten Carbonate</td>
<td>Ceramic</td>
</tr>
<tr>
<td>Operating Temperature</td>
<td>80°C</td>
<td>65°C - 220°C</td>
<td>205°C</td>
<td>650°C</td>
<td>600-1000°C</td>
</tr>
<tr>
<td>Charge Carrier</td>
<td>H⁺</td>
<td>OH⁻</td>
<td>H⁺</td>
<td>CO₃⁻</td>
<td>O⁻</td>
</tr>
<tr>
<td>External Reformer for CH₄ (below)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Prime Cell Components</td>
<td>Carbon-based</td>
<td>Carbon-based</td>
<td>Graphite-based</td>
<td>Stainless based</td>
<td>Ceramic</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Nickel</td>
<td>Perovskites</td>
</tr>
<tr>
<td>Product Water Management</td>
<td>Evaporative</td>
<td>Evaporative</td>
<td>Evaporative</td>
<td>Gaseous Product</td>
<td>Gaseous Product</td>
</tr>
</tbody>
</table>

### Aluminum - Oxygen semi-cell Solid Oxide Cell

\[
4\cdot\text{Al} + 6\cdot\text{H}_2\cdot\text{O} + 3\cdot\text{O}_2 \rightarrow 4\cdot\text{Al} \cdot (\text{OH})
\]

Al consumption: \[
0.62 \frac{\text{lbf}}{\text{kW.hr}} = 0.281 \frac{\text{kgf}}{\text{kW.hr}}
\]

O₂ consumption: \[
0.58 \frac{\text{lbf}}{\text{kW.hr}} = 0.263 \frac{\text{kgf}}{\text{kW.hr}}
\]

H₂O + KOH voltage: 1.4 - 1.5 V per cell

**Fuel Cell Technologies, Ltd**

(formerly Alupower)

(http://www.fct.ca)
**simplified model of Stirling cycle**

Closed; constant mass, states at end points shown; drive rotates $\pi/2$ clockwise between each state

Compare with continuous plot below. Volumes are designated 0, 0.5 and 1.0 to go with min, midway and max in each cylinder.

State 1:

\[
\begin{align*}
\text{vol}_{\text{hot}} &= 0.5 \\
\text{vol}_{\text{cold}} &= 1.0 \\
\text{vol}_{\text{total}} &= 1.5
\end{align*}
\]

Action 1 - 2: working fluid is compressed with $T = \text{constant}$, negative work done and heat is removed.

State 2:

\[
\begin{align*}
\text{vol}_{\text{hot}} &= 0.0 \\
\text{vol}_{\text{cold}} &= 0.5 \\
\text{vol}_{\text{total}} &= 0.5
\end{align*}
\]

Action 2 - 3: ~ constant volume, heat added to system from regenerator, note that end state volume is the same but what was in cold cylinder (2) goes to the hot (3).

State 3:

\[
\begin{align*}
\text{vol}_{\text{hot}} &= 0.5 \\
\text{vol}_{\text{cold}} &= 0.0 \\
\text{vol}_{\text{total}} &= 0.5
\end{align*}
\]

Action 3 - 4: working fluid is expanded with $T = \text{constant}$, positive work done and heat is added.

State 4:

\[
\begin{align*}
\text{vol}_{\text{hot}} &= 1.0 \\
\text{vol}_{\text{cold}} &= 0.5 \\
\text{vol}_{\text{total}} &= 1.5
\end{align*}
\]

Action 4 - 1: ~ constant volume, heat removed from system to regenerator, note that end state volume is the same but is in hot cylinder vs. cold.

12/11/2006
volume plot data

plot shows volume in cylinders and thermodynamic model with rotation

Stirling Cycle thermodynamic analysis

* The ideal Stirling cycle is made up of four totally reversible processes:
1-2 Constant temperature compression (heat rejection to external sink)
2-3 Constant volume regeneration (internal heat transfer from regenerator back to the working fluid).
3-4 Constant temperature expansion (heat addition from external source)
4-1 Constant volume regeneration (internal heat transfer from the working fluid to regenerator)

from gas relationships

\[ p \cdot v = R \cdot T \]  \hspace{1cm} (3.2)

\[ \frac{p_1 \cdot v_1}{T_1} = \frac{p_2 \cdot v_2}{T_2} \]  \hspace{1cm} (3.5)

\[ W_{1-2} = \int_{V_1}^{V_2} p \, dV = \int_{V_1}^{V_2} \frac{1}{V} \, dV = p_1 \cdot V_1 \cdot \ln \left( \frac{V_2}{V_1} \right) \]  \hspace{1cm} (4.5)

\[ s_2 - s_1 = c_{vo} \cdot \ln \left( \frac{T_2}{T_1} \right) + R \cdot \ln \left( \frac{v_2}{v_1} \right) \]  \hspace{1cm} (7.24)

\[ s_2 - s_1 = c_{po} \cdot \ln \left( \frac{T_2}{T_1} \right) - R \cdot \ln \left( \frac{p_2}{p_1} \right) \]  \hspace{1cm} (7.23)

\[ du = c_{vo} \cdot dT \]  \hspace{1cm} \text{constant volume}  \\
\[ v_0 \]  \hspace{1cm} \text{ideal gas}  \hspace{1cm} (5.20)

kJ := 10^3 \cdot \text{J}

kmol := 10^3 \cdot \text{mole}
Data for example:
again, parameterize in terms of \( p_1 < p < p_3 \), given ...
\[ c_{v_0} = \text{constant} \quad c_{p_0} = \text{constant} \]
insert \( N_2 \) values e.g.: \( \text{mw}_{N_2} := 28 \ \text{kg/kmol} \)

\[ \begin{align*}
T_H &:= 1000 \text{K} & p_1 &:= 1 \text{bar} & N_2 &:= \ \text{kg} \\
T_L &:= 300 \text{K} & c_p &:= 1.042 \ \text{kJ/kg\cdot K} & R_m &:= 8.3144 \ \text{kJ/kmol\cdot K} & R &:= \frac{R_m}{\text{mw}_{N_2}} = R = 0.297 \ \text{kJ/kg\cdot K} \\
\end{align*} \]

\( v_1 := \frac{R \cdot T_L}{p_1} \quad v_1 = 0.891 \ \text{m}^3/\text{kg} \quad \gamma := 1.4 \quad c_v := \frac{c_p}{\gamma} \quad c_v = 0.744 \ \text{kJ/kg\cdot K} \)

\( T_1 := T_L \quad P \cdot V = R \cdot T \)

\( s_1 := 1 \ \text{kJ/kg\cdot K} \quad r := 3 \quad \text{compression ratio} \quad \text{ten increments for plotting} \quad \text{NN} := 10 \quad i := 0..\text{NN} \)

1 - 2 compression, constant internal energy, heat rejection at constant temperature (negative) work done
\[ p \cdot v = R \cdot T \quad p_1 < p < p_2 \quad p_2 := r \cdot p_1 \quad p_2 = 3 \text{ bar} \]
incremental for plots
\[ \begin{align*}
p_{1,2,0} &:= \frac{p_2 - p_1}{\text{NN}} + p_1 \quad v_{1,2,0} := \frac{R \cdot T_1}{p_{1,2,0}} \quad \frac{v_{1,2,0}}{v_{1,2,10}} = 3 \quad T_2 := T_1 \quad v_2 := v_{1,2,\text{NN}} \quad v_2 = 0.297 \ \text{m}^3/\text{kg} \\
\end{align*} \]

\[ w_{1,2} = \int_{1}^{2} p \ dv = R \cdot T_1 \int_{1}^{2} \frac{1}{v} \ dv = R \cdot T_1 \cdot \ln \left( \frac{v_2}{v_1} \right) \quad w_{1,2} := R \cdot T_1 \cdot \ln \left( \frac{v_2}{v_1} \right) \quad w_{1,2} = -97.868 \ \text{kJ/kg} \]

first law, mass constant \( c_v \), \( T \) constant \( \Delta H \) 1 - 2 = 0
\[ q_{1,2} = w_{1,2} = R \cdot T_1 \cdot \ln \left( \frac{v_2}{v_1} \right) = T_1 (s_2 - s_1) \quad q_{1,2} := w_{1,2} \quad q_{1,2} = -98 \ \text{kJ/kg} \quad s_2 := \frac{q_{1,2}}{T_1} + s_1 \quad s_2 = 0.674 \ \text{kJ/kg} \]

\( \text{plot 1 - 2} \)

2 - 3 constant volume heat addition (from regenerator)
\[ p \cdot v = R \cdot T \]
\[ q_{2,3} := c_v(T_H - T_L) \quad q_{2,3} = 521 \ \text{kJ/kg} \]
\[ v_3 := v_2 \quad T_3 := T_H \]
\[ p_3 := \frac{R \cdot T_3}{v_3} \quad p_3 = 10 \text{ bar} \quad T_{2,3}(p_{2,3}) = \frac{p_3 \cdot v_2}{R} \quad s_{2,3}(p_{2,3}) = s_2 + c_v \cdot \ln \left( \frac{T_{2,3}(p_{2,3})}{T_2} \right) \]

functionally
\[ s_2 - s_1 = c_{v_0} \cdot \ln \left( \frac{T_2}{T_1} \right) + R \cdot \ln \left( \frac{v_2}{v_1} \right) \]
(7.24)

incremental for plots
\[ \begin{align*}
p_{2,3,1} &:= p_2 + \frac{p_3 - p_2}{\text{NN}} \quad T_{2,3,1} := \frac{p_{2,3,1} \cdot v_2}{R} \quad s_{2,3,1} := \left( s_2 + c_v \cdot \ln \left( \frac{T_{2,3,1}}{T_2} \right) \right) \quad \text{indicially} \quad s_3 := s_{2,3,\text{NN}} \quad s_3 = 1.57 \ \text{kJ/kg\cdot K} \\
\end{align*} \]

\( \text{plot 2 - 3} \)

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3 - 4 (+) work done by fluid; expansion at constant internal energy, heat addition; at constant temperature

constant volume ... \( v_4 := v_1 \)

constant temperature \( T_4 := T_H \)

\( v_4 = 0.891 \text{ m}^3 / \text{kg} \)

\[ p \cdot v = R \cdot T \]

\( p_3 = 10 \text{ bar} \)

\( p_4 := \frac{R \cdot T_4}{v_4} \)

\( p_4 = 3.333 \text{ bar} \)

\( p_2 = 3 \text{ bar} \)

\( p_3 \cdot 4_i := \frac{p_4 - p_3}{NN} \cdot i + p_3 \)

\( v_{3 \cdot 4_i} := \frac{R \cdot T_3}{p_{3 \cdot 4_i}} \)

\( v_{3 \cdot 0} := \frac{R \cdot T_3}{v_{3 \cdot 10}} = 0.333 \)

\( w_{3 \cdot 4} = \int_3^4 p \, dv = R \cdot T_3 \cdot \ln \left( \frac{v_4}{v_3} \right) \]

\( w_{3 \cdot 4} := R \cdot T_3 \cdot \ln \left( \frac{v_4}{v_3} \right) \)

\( w_{3 \cdot 4} = 326 \text{ kJ/kg} \)

\( q_{3 \cdot 4} = w_{3 \cdot 4} = R \cdot T_3 \cdot \ln \left( \frac{v_4}{v_3} \right) = T_3 \cdot (s_4 - s_3) \)

\( q_{3 \cdot 4} := w_{3 \cdot 4} \)

\( s_4 := \frac{q_{3 \cdot 4}}{T_3} + s_3 \)

\( s_4 = 1.896 \text{ kJ/kg K} \)

4 - 1 constant volume heat rejection, via regenerator

\[ p \cdot v = R \cdot T \]

\( T_1 = 300 \text{ K} \)

\( q_{4 \cdot 1} := c_v (T_1 - T_4) \)

\( q_{4 \cdot 1} = -521 \text{ kJ/kg} \)

\( v_{4 \cdot 1} := v_4 \)

\( T_{4 \cdot 1} := T_L \)

\( p_{4 \cdot 1} := \frac{R \cdot T_1}{v_1} \)

\( p_{4 \cdot 1} := p_4 + \frac{p_1 - p_4}{NN} \cdot i \)

\( T_{4 \cdot 1} := \frac{p_{4 \cdot 1} \cdot v_4}{R} \)

\( p_1 = 1 \text{ bar} \)

\( s_{4 \cdot 1} := s_4 + c_p \cdot \ln \left( \frac{T_{4 \cdot 1}}{T_4} \right) - R \cdot \ln \left( \frac{p_{4 \cdot 1}}{p_4} \right) \)

\( s_{4 \cdot 1} \text{ indicially} \)

\( s_4 := s_{4 \cdot NN} \)

\( s_1 = 0.999 \text{ kJ/kg K} \)

Here could have used \( c_v \) relationship as well. Both are consistent as the area will show

Set up plot
\[ \eta_{th} := \frac{w_{3\,4} + w_{1\,2}}{q_{3\,4}} \quad \eta_{th} = 0.7 \quad \eta_{th\,carnot} := 1 - \frac{T_L}{T_H} \quad \eta_{th\,carnot} = 0.7 \]
for closed cycle combustion ....

c_{12}\text{H}_{26} + 18.5\text{O}_2 + 69.6\text{N}_2 = 13\text{H}_2\text{O} + 12\text{C}\cdot\text{O}_2 + 69.6\text{N}_2 + \text{heat}

\begin{align*}
\text{mw}_\text{O}_2 & := 32 \frac{\text{kg}}{\text{kmol}} & \text{mw}_\text{C}_{12}\text{H}_{26} & := (144 + 26) \frac{\text{kg}}{\text{kmol}} & \text{mw}_\text{N}_2 & := 28 \frac{\text{kg}}{\text{kmol}} \\
\text{mw}_\text{H}_2\text{O} & := (2 + 16) \frac{\text{kg}}{\text{kmol}} & \text{mw}_\text{C}_2 \text{O}_2 & := (12 + 32) \frac{\text{kg}}{\text{kmol}}
\end{align*}

1\text{kmol} \text{c}_{12}\text{H}_{26} + 18.5\text{kmol}\cdot\text{O}_2 + 69.6\text{kmol}\cdot\text{N}_2 = 13\text{kmol}\cdot\text{H}_2\text{O} + 12\text{kmol}\cdot\text{C}\cdot\text{O}_2 + 69.6\text{kmol}\cdot\text{N}_2 + \text{LHV}

\begin{align*}
\left( \frac{1\text{kmol}\cdot\text{mw}_\text{C}_{12}\text{H}_{26}}{170} \right) \cdot \text{c}_{12}\text{H}_{26} & = \left( \frac{13\cdot\text{kmol}\cdot\text{H}_2\text{O}}{170} \right) \cdot \text{H}_2\text{O} + \left( \frac{12\text{kmol}\cdot\text{C}_2\text{O}_2}{170} \right) \cdot \text{C}_2\text{O}_2 + \left( \frac{69.6\text{kmol}\cdot\text{N}_2}{170} \right) \cdot \text{N}_2 \\
\text{and this is divided by 170 - the molecular weight of c}_{12}\text{H}_{26} to express on a per 1 kg fuel basis}
\end{align*}

\begin{align*}
\text{weight of air : weight of fuel} = \text{air-fuel ratio} & \\
\eta = \frac{\text{kW}}{\text{m}_\text{f}\cdot\text{dot}\cdot\text{LHV}} & \text{sfc} = \frac{\text{m}_\text{f}\cdot\text{dot}}{\text{kW}}
\end{align*}

\begin{align*}
\text{LHV} & := 43000 \frac{\text{kJ}}{\text{kg}} & \text{m}_\text{f}\cdot\text{dot} & := 1 \frac{\text{kg}}{\text{s}}
\end{align*}

\text{power} := 10000\text{kw}

\begin{align*}
\eta & := \frac{\text{power}}{\text{m}_\text{f}\cdot\text{dot}\cdot\text{LHV}} & \eta & := 0.233 & \text{sfc} & := \frac{\text{m}_\text{f}\cdot\text{dot}}{\text{kW}} & \text{sfc} & := 3.6 \times 10^3 \frac{\text{kg}}{\text{kW}\cdot\text{hr}}
\end{align*}