Thermodynamic Analysis of an Electrochemical Refrigeration Cycle

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ABSTRACT

The coupling of a water-based electrochemical cell and fuel cell are discussed as a means to form a refrigeration cycle. In the proposed configuration, the process fluids can be passively driven through the flow circuits. The cycle requires low direct current voltages for driving the cycle. Current densities must be maintained sufficiently low in the electrochemical cell in order to operate below neutral voltage levels. Overall, the cycle's operational limit for the configuration described is close to Carnot efficiency.

INTRODUCTION

A fuel cell and its reversible analog, the electrochemical cell, can be coupled in a manner that forms some interesting thermodynamic cycles. A simple thermodynamic analysis of a configuration for a refrigeration cycle is described in this paper. Alternative configurations can also be developed for achieving refrigeration effects and for forming thermally driven power cycles.

Fuel cells and electrochemical cells have a long history in science and in application (Soo (1968)). Industrial electrochemical processes are responsible for the production of many materials. Research in the fuel cell area continues to grow with significant demonstrations of the technology showing its future potential (Appleby and Foulkes (1989)). Thermodynamic processes are understood and basic fuel cell analyses commonly appear in thermodynamic textbooks (e.g., Moran and Shapiro (1995), Howell and Buckius (1992)). Several areas of difficulties related to materials, transport processes and cost must be addressed in order to determine whether a practical system of the type described could be developed. Ohta (1979) and Casper (1978) discuss many fuel cell and electrochemical performance issues.

CYCLE DESCRIPTION

Figure 1 is a schematic of the proposed cycle. Four primary components make up the system. An electrochemical cell is the heat absorber, equivalent to an evaporator in a conventional vapor compression refrigeration system. A fuel cell rejects heat in a manner similar to a condenser in a common vapor compression refrigeration cycle. The third component is a heat exchanger between gas streams and water flow stream. The fourth component is a current pump for elevating the fuel cell's voltage output to a level sufficient for driving the electrochemical cell. The voltage required is sufficiently low such that the cycle may be one that is conveniently matched for solar
photovoltaic cells or other direct current electric energy conversion systems. It should be noted that the system shown in Figure 1 can be used as a thermally driven power cycle by operating the fuel cell at a temperature lower than the electrochemical cell. In this case, the voltage supply becomes a load driven by the electric circuit.

The system is assumed to be based on a water/hydrogen/oxygen fuel cell and electrochemical cell combination. Other combinations may also be considered. For example, sodium chloride highly concentrated in water would produce chlorine and oxygen in the electrochemical cell. An aqueous solution of sodium chloride and sodium hydroxide would be passed to the fuel cell for the reversed chlorine/oxygen reaction. Possible advantages or disadvantages of this or other alternative working fluids are not considered in this work.

The configuration envisioned for the system shown in Figure 1 operates near atmospheric pressure. The components could be operated at nearly uniform pressures with gravitation and/or surface tension used for transporting the working fluids within and between components. Water may be moved from the electrochemical cell and fuel cell to external heat exchange surfaces, or, the cells could be configured for direct heat exchange with their surroundings.

![Figure 1](image)

Figure 1 Schematic of an electrochemical absorption refrigeration cycle. The electrochemical cell is the heat absorber and the fuel cell the heat rejector.
CYCLE ANALYSIS

Basic forms of the 1st and 2nd Laws of thermodynamics are used to model each of the system's components. Fuel cell work transfer can be described by the following relation.

\[ W_f = n_{H_2O} \left( T_1 \left( h_{H_2O_e} - h_{H_2O_i} \right) \right) - n_{H_2} \left( T_1 \left( h_{H_2} - h_{H_2e} \right) \right) - n_{O_2} \left( T_1 \left( h_{O_2} - h_{O_2e} \right) \right) - T_1 S_{ge} \quad (1) \]

Figure 2 shows a schematic of the fuel cell system and its flow streams. The work is in the form of electrical current flow. The fuel cell is assumed to operate at the temperature of its surrounding environment. Property values for the incoming hydrogen and oxygen streams are assumed to be at the fuel cell operating temperature, \( T_1 \), the heat exchanger's performance limit.

A similar relation can be written for the electrochemical cell's work.

\[ W_e = -n_{H_2O} \left( T_2 \left( h_{H_2O_i} - h_{H_2O_e} \right) \right) + n_{H_2} \left( T_2 \left( h_{H_2} - h_{H_2e} \right) \right) + n_{O_2} \left( T_2 \left( h_{O_2} - h_{O_2e} \right) \right) - T_2 S_{ge} \quad (2) \]

Figure 3 shows a schematic of the electrochemical cell system. The cell work input is in the form of electrical current flow. The electrochemical cell is assumed to operate at the temperature of its surrounding environment, \( T_2 \). Water flowing into the electrochemical cell enters at a temperature somewhat elevated above the cell temperature due to thermodynamic limitations in the heat exchanger located between the two cells.

Heat transfer for the fuel cell and the electrochemical cell are found from a 1st Law energy balance. These relations are shown in equations 3 and 4, respectively.

\[ Q_f = n_{H_2O} h_{H_2O_e} - n_{H_2} h_{H_2i} - n_{O_2} h_{O_2i} + W_f \quad (3) \]

\[ Q_e = -n_{H_2O} h_{H_2O_i} + n_{H_2} h_{H_2e} + n_{O_2} h_{O_2e} + W_e \quad (4) \]

A heat exchanger is used in order to exchange energy between the low temperature gas streams and the higher temperature water stream. As will be shown later, because water's heat capacity is greater than that of the combined oxygen and hydrogen streams, the gas streams can exit at the water's inlet temperature in the limiting case. Water exiting from the exchanger cannot reach the gas streams' entering temperature. Figure 4 is a schematic of the heat exchanger system. A 1st Law analysis for the heat exchanger is:

\[ 0 = n_{H_2O} \left( h_{H_2O_i} - h_{H_2O_e} \right) + n_{H_2} \left( h_{H_2i} - h_{H_2e} \right) + n_{O_2} \left( h_{O_2i} - h_{O_2e} \right) \quad (5) \]

This set of relations is sufficient for finding the cycle efficiency when given system operating temperatures and pressures for the fuel cell and electrochemical cell. A simplified set of relations can be developed that takes advantage of the gas stream components' ideal gas nature and the water stream's liquid characteristics. Utilizing these characteristics allows the system's operating
temperatures and pressures to be used directly in the governing equations. The work relations for the fuel cell and the electrochemical cell can be rewritten as:

\[
\begin{align*}
\text{w}_f &= [T_1 (s_{H_2O} + c_{H_2O} \ln(T_1/298K)) - (h_{H_2O} + c_{H_2O} (T_1-298K))] \quad (6) \\
&\quad - [T_1 (s_{H_2O} + c_{H_2} \ln(T_1/298K) - R \ln(P_1/1atm)) - c_{H_2} (T_1-298K)] \\
&\quad - 0.5[T_1 (s_{O_2} + c_{O_2} \ln(T_1/298K) - R \ln(P_1/1atm)) - c_{O_2} (T_1-298K)] \\
\text{w}_c &= - [T_2 (s_{H_2O} + c_{H_2O} \ln(T_2*/298K)) - (h_{H_2O} + c_{H_2O} (T_2*-298K))] \quad (7) \\
&\quad + [T_2 (s_{H_2O} + c_{H_2} \ln(T_2/298K) - R \ln(P_2/1atm)) - c_{H_2} (T_2-298K)] \\
&\quad + 0.5[T_2 (s_{O_2} + c_{O_2} \ln(T_2/298K) - R \ln(P_2/1atm)) - c_{O_2} (T_2-298K)]
\end{align*}
\]

Reversibility has been assumed in equations 6 and 7 because the operational limits of the cycle are to be analyzed. Standard state enthalpies for oxygen and hydrogen are zero. Water's standard state enthalpy is assumed to be in the liquid state for the temperatures and pressures considered for system operation. Note that the gas pressures are total pressures because the gas streams enter and exit the fuel cell and electrochemical cell separated at the component operating pressures.

Equations 3 and 4 using ideal gas and liquid water characteristics are:

\[
\begin{align*}
q_f &= h_{H_2O} + c_{H_2O} (T_1-298K) - c_{H_2} (T_1-298K) - 0.5 c_{O_2} (T_1-298K) + w_f \quad (8) \\
q_c &= - h_{H_2O} - c_{H_2O} (T_2*-298K) + c_{H_2} (T_2-298K) + 0.5 c_{O_2} (T_2-298K) + w_c \quad (9)
\end{align*}
\]

When specific heat relations are substituted into equation (5) for the heat exchanger, an expression is obtained for water's exiting temperature. This expression is based on observing that both hydrogen and oxygen specific heats are less than that of liquid water, indicating that water must exit at some temperature higher than the inlet gas temperature.

\[
T_2^* = T_1 - (c_{H_2} + 0.5 c_{O_2}) (T_1 - T_2) / c_{H_2O} \quad (10)
\]

Water's elevated temperature at the heat exchanger is a source of irreversibility.

Equations 6 through 10 can be solved for the work and heat transfers, and for the water exit temperature from the exchanger for a given set of operating temperatures and pressures.
Figure 2  Schematic of the fuel cell system analyzed. The fuel cell is assumed to operate at the temperature of its ambient surrounds. Inlet and outlet flows are at the same temperature as the cell operating temperature.

Figure 3  Schematic of the electrochemical cell system analyzed. The cell is assumed to operate at the temperature of its ambient surrounds. Outlet flows are at the same temperature as the cell operating temperature. The inlet water flow, due to thermodynamic limitations in the heat exchanger, enters at temperature $T_2^*$. 

Figure 4  Schematic of the heat exchanger system between hydrogen, oxygen, and water flows. The exchanger is assumed to operate at its thermodynamic limit allowing the oxygen and hydrogen to exit at the water stream's inlet temperature.
RESULTS

Conditions have been assumed for operating the cycle for air conditioning. A range of cold side temperatures from 273K to 318K have been used with the warm side of the cycle at 323K and 333K. Entropy generation in the fuel cell and electrochemical cell have been assumed to be zero in order to observe operational performance limits. All cycle components are assumed to operate at atmospheric pressure. Standard state property values and specific heat values have been taken from a standard thermodynamics textbook (Moran and Shapiro (1995)). Variation of the cycle's refrigeration coefficient of performance, heat transfer, work, and voltage levels have been determined.

Figure 5 shows the variation of the cycle's coefficient of performance (COP) for two different fuel cell operational temperatures. The low temperature conditions of the electrochemical cell have been varied from 273K to 318K. The COPs are within one percent of the COP of a fully reversible cycle, indicating that the irreversibility from the heat exchanger is not significant.

![Refrigeration COP for the electrochemical system over a range of low temperatures (electrochemical cell temperatures) and two high temperatures (fuel cell temperatures).](image)

Figure 6 shows the fuel cell and electrochemical cell heat transfers over a range of cold-side temperatures. The fuel cell's heat transfer per mass of water increases with increasing operational temperature. The electrochemical cell's heat transfer is relatively unaffected by the fuel cell's operational temperature. The opposite is also true. That is, the electrochemical cell's operational condition is relatively unaffected by the fuel cell's temperature. The primary factor that links the performance of the two cells is the heat exchanger. Because the heat capacities between the water
and gas streams are not perfectly matched, variation of the fuel cell and electrochemical cell operational temperatures affects the water temperature that enters the electrochemical cell. The mismatch, however, results in a small irreversibility to the overall system. Figure 7 shows the variation of the water outlet temperature from the heat exchanger relative to the operational temperatures of the fuel cell and electrochemical cell.

**Figure 6**  Electrochemical cell and fuel cell absolute heat transfer per water mass for two fuel cell temperatures over a range of electrochemical cell temperatures.

**Figure 7**  Plot of the water outlet temperature from the heat exchanger relative to the fuel cell and electrochemical cell temperatures.
Figure 8 shows the work required by the electrochemical cell and the work produced by the fuel cell. The fuel cell's work output is reduced as its temperature is increased. The work produced by the fuel cell is lower than the work required by the electrochemical cell. As the electrochemical cell's temperature approaches the fuel cell's temperature, the work difference is reduced to zero.

![Diagram showing the work required by the electrochemical cell and the work produced by the fuel cell.](image)

Figure 8: Electrochemical cell and fuel cell work per water mass for two fuel cell temperatures over a range of electrochemical cell temperatures.

Figure 9 shows the voltages across the fuel cell and the electrochemical cell for the assumed range of conditions. Voltages are determined by calculating the current flow per mole of water. The current, relative to the work per mole in the fuel cell and electrochemical cell, determines the voltage across each cell.

Irreversibilities in the fuel cell and electrochemical cell affect the system operation in different manners. Irreversibilities, in general, lower the cycle's performance. In the fuel cell, a lower voltage output occurs, thus requiring a larger voltage boost for driving the electrochemical cell. Irreversibilities in the electrochemical cell affect the cycle in two ways. First, the voltage required to operate the cell increases. The second, and more significant effect, is internal heat generation that limits the amount of heat transferred into the electrochemical cell from its surroundings. When the level of irreversibility increases sufficiently, a "neutral" voltage level is reached. This is the limit where no external heat transfer occurs. Above the neutral voltage limit, the electrochemical cell exhausts thermal energy to its surroundings. Ohta (1978) describes the types of irreversibilities within hydrogen/oxygen electrolysis systems.
The operational limit of the cycle, when irreversibilities in the electrochemical cell reach the neutral voltage level, can be determined by setting the electrochemical cell's heat transfer to zero. The entropy generation term is included in the electrochemical cell's work relation, or alternatively, the cell's reversible work can be divided by an efficiency parameter. Figure 10 shows the electrochemical cell efficiency when irreversibilities cause the cell to operate at the neutral voltage level. When cell efficiencies are below those shown in Figure 10, the system can no longer operate in the refrigeration mode. The actual neutral voltage level is insensitive to the operational conditions shown in Figure 10. The neutral voltage varies between 1.476 and 1.478 volts for the conditions plotted. Brown, et.al. (1980) describe electrode surfaces with low overvoltage characteristics. Current densities less than 10 milliamps per square centimeter may be operated with overvoltages that are 0.01 volts above the reversible limit.

The mass flow rate for achieving a desired level of refrigeration is shown in Figure 11. Water flow rates for one "ton" (12,000 Btu/hr = 12,600 kJ/hr) of refrigeration is plotted over a range of cell temperatures with reversible cell operation assumed. One ton of refrigeration is typical of room air conditioners (window units). Mass flows are sensitive to the electrochemical cell's temperature, however, the fuel cell's temperature is not as significant.

All results presented have assumed that the system operates uniformly at atmospheric pressure. Variation of the system's pressure does not significantly affect the performance values shown in the previous figures as long as a uniform pressure is assumed throughout the system. A
configuration which relies on surface tension or gravitational bases for moving fluids between system components has been assumed. Unrestrained pressure drops between the components will lead to irreversibilities that adversely affect system performance.

Figure 10 Minimum electrochemical cell efficiency over a range of operating conditions.

Figure 11 Water flow per "ton" of refrigeration capacity over a range of operational conditions.
CONCLUSIONS

A method for operating a refrigeration cycle has been described. Practical development of the system depends on several factors. High quality electrode surfaces must be used in order to keep voltage drops and reaction resistances to a minimum. Electrolytes for the fuel cell and electrochemical cell must be chosen. The costs associated with these components is another factor affecting the economic feasibility of the proposed system.

A beneficial aspect of the proposed system is that it may be coupled to a variety of low voltage, direct current electrical energy generators. Photovoltaic solar cells would be one example of an energy source that may be directly compatible with the "current pumping" required by this system. Cell modules would need to be "stacked" in a series configuration in order to have the overall voltage differential match the voltage level available for driving the system. Stacking cell modules is also desirable in order to keep current flow, and therefore electric circuit resistive losses small.

Environmentally, the system is free of refrigerant compounds with ozone depletion and global warming concerns. Safety issues regarding the movement of oxygen and hydrogen must be address, however, the mass flow rates are quite small per ton of refrigeration effect and reasonable designs should be able to minimize the actual system mass and volume in hydrogen and oxygen.
NOMENCLATURE

c_{O2}  molar constant pressure specific heat of oxygen

c_{H2}  molar constant pressure specific heat of hydrogen

c_{H2O} molar constant pressure specific heat of water

h_{O2}  molar enthalpy of oxygen

h_{H2}  molar enthalpy of hydrogen

h_{H2O} molar enthalpy of water

n_{O2}  moles of oxygen transported

n_{H2}  moles of hydrogen transported

n_{H2O} moles of water transported

Q_c  electrochemical cell heat transfer

Q_f  fuel cell heat transfer

q_c  electrochemical cell heat transfer per mole of water

q_f  fuel cell heat transfer per mole of water

R  universal gas constant

s_{O2}  molar entropy of oxygen

s_{H2}  molar entropy of hydrogen

s_{H2O} molar entropy of water

S_{gc}  entropy generation in the fuel cell

S_{gf}  entropy generation in the fuel cell

T_1  fuel cell operating temperature

T_2  electrochemical cell operating temperature

T_2*  water outlet temperature from the heat exchanger

W_c  electrochemical cell work

W_f  fuel cell work

w_c  electrochemical cell work per mole of water

w_f  fuel cell work per mole of water

superscript

^0  indicates property (enthalpy or entropy) at standard state value (1 atmosphere and 298K)

subscripts

i  indicates inlet stream to the system of interest

e  indicates an exit stream from the component of interest
REFERENCES


