Clarifying reversible efficiency misconceptions of high temperature fuel cells in relation to reversible heat engines

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Abstract

High temperature fuel cells are promising energy conversion devices. Optimal design and analysis require a thorough understanding of their second law limitations. Fuel cells do not produce work from thermal energy as do heat engines. This has led to the provocative statement that fuel cells are 'non-Carnot limited'. This label easily, yet erroneously, connotes that an ideal fuel cell is *superior* to an externally reversible heat engine. Clarity is achieved by analyzing the corresponding *systems* of these technologies. Conventional reversible fuel cell efficiency is also addressed, and a modified relation is developed. It accounts for the needed coupling of high temperature fuel cells with reversible heat engines, in order for maximum work to be produced. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Fuel cells are direct energy conversion systems. They partially convert the Gibbs free energy release of fuel (typically hydrogen) and oxidant into electricity via electrochemical reactions. This controlled oxidation fosters higher energy conversion efficiency and lower emissions than in the case of combustion power systems.

An illustration of a fuel cell is given in Fig. 1. High temperature fuel cells have distinct advantages. High temperature fuel cells include molten carbonate and solid oxide fuel cells. Their elevated temperatures preclude the need for expensive electrode catalysts. Several fossil fuels may be used as raw (i.e. pre-processed) fuel. Finally, the thermal energy rejected by the fuel cells is of high quality. The *quality* of heat flow is the fraction that can become useful power. There has been interest on behalf of the United States Department of Energy, Federal Energy Technology Center (USDOE FETC) in using high temperature fuel cells as topping units within gas turbine cycles [1]. Such hybrid systems are predicted to reach electric efficiencies of 70% or higher [2].

Full clarity about *ideal* fuel cell operation is a precursor to effective analysis of non-ideal cells, as with many energy conversion devices. An example is how a thorough understanding of the Carnot cycle facilitates heat engine evaluation. Two common statements made about fuel cells are that they are 'non-Carnot limited' and that their maximum efficiency is the ratio of the Gibbs free energy of reaction to the corresponding enthalpy of reaction (the typical reaction is hydrogen oxidation).

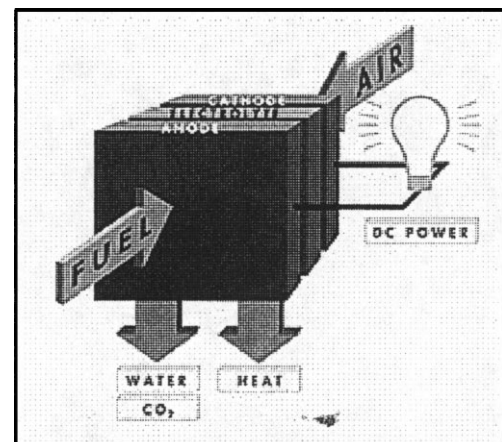$$\eta_{ideal} = \frac{\Delta G}{\Delta H} \qquad (1)$$

Fig. 1. Illustration of electrochemical principles associated with fuel cells.

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Nomenclature

a	Molar specific availability
g	Molar specific Gibbs free energy
G	(Extensive) Gibbs free energy
h	Molar specific enthalpy
H	(Extensive) enthalpy
$\dot{n}$	Molar flow rate
p	Pressure
$\dot{Q}$	Heat
s	Molar specific entropy
T	(Absolute) temperature
$\dot{W}$	Power

Greek

Δ	'Change in'
η	Efficiency
μ	Chemical potential
ν	Stoichiometric coefficient
Σ	Summation

These assertions are examined for a lucid understanding of their implications. The latter assertion has been modified in consideration of bottoming cycles.

2. The 'non-Carnot limited' label

2.1. Issue

Fuel cells do not utilize heat to produce work; they generate both work and heat from electrochemical fuel oxidation. A number of references thus indicate fuel cells are non-Carnot limited. An example is that of Cengel and Boles [3]. "Fuel cells are not heat engines, and thus their efficiencies are not limited by the Carnot efficiency." Fuel cells are 'non-Carnot limited' in that their operation is not a function of temperature reservoirs, but one must be careful not to conclude that an ideal fuel cell is a *better energy converter* than is a Carnot cycle. Both units are perfect energy conversion devices that conserve the supply of *exergy* received by them.

2.2. Thermodynamic comparison of a reversible fuel cell and reversible heat engine

A figure or merit of an energy system is how well it conserves the *exergy* supplied to it. Notice the operative term is *exergy*, since energy is conserved in any process [4]. Exergy is work potential, and it *can* be destroyed via irreversibilities.

An ideal fuel cell and an externally reversible heat engine are illustrated in Fig. 2. Both systems are supplied energy flows with the same availability (or exergy) 'A'.

$$\text{Availability}_A = \sum_i (\dot{n}_i a_i)_{\text{inlet, fuel cell}} = \left[1 - \frac{T_o}{T_H} \right] \dot{Q}_H \qquad (2)$$

Waste streams availability 'B' is zero, meaning all of availability 'A' has been converted. Consider both energy conversion systems to be reversible thermodynamic 'black boxes'. Both systems must have the same productivity. This is in compliance with the fact that maximum work is a point function. It depends on the availability supplied to a power system. To state that the ideal fuel cell is 'non-Carnot limited' in regard to its level of performance easily, yet erroneously, implies that reversible energy conversion (between given end states) is path dependent and not a state function. Notice the perfect heat engine of Fig. 2 receives *heat* and not *chemical fuel*. Most references which state that fuel cells have better performance than Carnot cycles are making the comparison in regard to both systems being fed the same chemical reactants. This type of comparison, however, forces an artificial link between Carnot cycles and combustion irreversibility.

Cownden et al. [5] state, "...because a fuel cell utilizes an electrochemical energy conversion process rather than *combustion*, its efficiency is not limited by that for a *corresponding* Carnot cycle...." It is inappropriate, however, to associate combustion to externally reversible heat engines in the discussion of 'Carnot' (not 'heat engine') efficiency. The operation of an externally reversible heat engine does not generate entropy. Combustion, however, is highly irreversible. As an important sidenote, this suggests a modification of the proof developed by Appleby [6]. He correctly concluded the equivalent performances between an ideal fuel cell and a Carnot cycle, understanding that both were
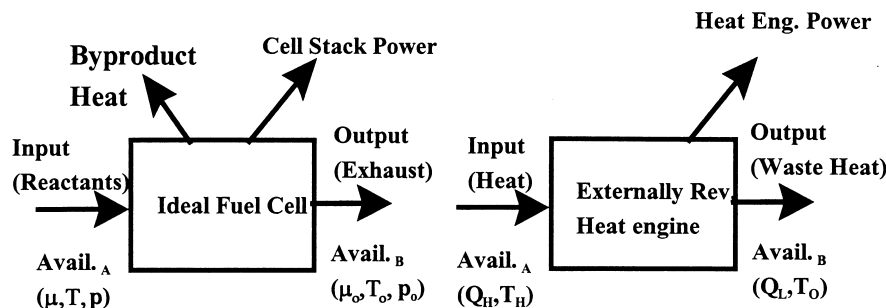

Fig. 2. Reversible fuel cell and heat engine.

'thermodynamic black boxes'. His proof, however, involves supplying both systems chemical reactants and allowing *spontaneous* combustion to occur in the latter, and culminates in an implicit statement that Carnot cycle efficiency is solely a function of the lower temperature reservoir (i.e. the value of Eq. (1) taken at the heat rejection temperature of the Carnot cycle). It is a requirement of the second law of thermodynamics, however, that all heat engines operate between, and be a function of, at least two temperature limits. For an appropriate comparison of the technologies, based on each receiving the same energy supply, a comparison is made between a fuel cell *system* and a heat engine *system*.

2.3. Comparison of a fuel cell system and a heat engine system

Thermodynamically, the comparison of technologies as proposed in Fig. 2 is appropriate. A more practical comparison, however, is to supply a fuel cell system and combustion power system the same fuel and oxidant, and compare the systems' productivities.

The information contained in Table 1 is the recommended means of comparison. Both systems are supplied hydrocarbon fuel (e.g. natural gas). The means of chemical energy release in the fuel cell system is the oxidation of the fuel *in stages*. The fuel is first steam reformed in a fuel processor (waste heat from the high temperature cell may supply thermal energy) so that it becomes a usable hydrogen-rich mixture. Next, controlled oxidation of reformate occurs electrochemically at the fuel cell anode. Conversely, the chemical reactions in the heat engine system are vigorous and spontaneous combustion. As discussed earlier, an ideal fuel cell and ideal heat engine do not generate entropy and so both are thermodynamically perfect. The power conditioning technologies have comparable efficiencies. The difference in fuel oxidation is thus the primary reason fuel cell *systems* are typically better energy converters than are heat engine *systems*. The 'non-Carnot limited' label should actually be a 'non-combustion limited' label, and it must not be construed to represent a direct comparison between an ideal fuel cell and an externally reversible heat engine. Dunbar et al. [7] highlight the lack of combustion irreversibility as the primary reason for the higher efficiencies of fuel cell *systems* and not the '*apparent* ... elimination of the Carnot-efficiency limitation.' The remaining misconception is that of the ideal fuel cell efficiency.

3. Ideal fuel cell efficiency

3.1. Issue

The productivity of high temperature fuel cells is not solely via direct energy conversion. The quality of heat rejected should also be considered and leads to a reconsideration of ideal fuel cell efficiency.

$$\eta_{\text{ideal}} = \frac{\Delta G}{\Delta H} = \frac{-\Delta G}{-\Delta H} \tag{3}$$

Eq. (3) is the conventional statement of reversible fuel cell efficiency. This first law index of performance is based upon the premise that an ideal fuel cell can foster no more work than the corresponding Gibbs free energy release from reactants to products (i.e. hydrogen and oxygen reacting to steam). The denominator represents the energy released during the reaction. Consider the full representation of the Gibbs free energy of reaction.

$$\Delta G = \sum_i v_i g_i \tag{4a}$$

$$g_i = h_i - T_i s_i \tag{4b}$$

Fuel cells are often thought to be isothermal systems in thermal equilibrium with the atmosphere [8]. The latter relation could thus be simplified.

$$g_i = h_i - T_o s_i \tag{4c}$$

The Gibbs free energy release is now the decrease in stream availability (exergy) from reactants to products, and the numerator of Eq. (3) does represent maximum work. The issue is that high temperature fuel cells operate at temperatures significantly greater than ambient.

3.2. Reconsideration of reversible efficiency in regard to high temperature cells

Molten carbonate fuel cells (650°C) and solid oxide fuel cells (1000°C) have received significant attention from entities such as the FETC for the high system efficiencies they can foster [9]. Their elevated temperatures preclude the

Table 1
Comparison of entire systems

	Fuel cell system	Heat engine system
Preparation of energy as needed by energy converter	Reforming hydrocarbon fuel to produce a hydrogen-rich gas mixture	Combusting hydrocarbon fuel to produce heat
Ideal energy conversion	Ideal fuel cell	Externally reversible heat engine
Power conditioning	Commutation (DC-AC)	Generator conversion of shaft power to AC electricity

substitution made in Eq. (4c) (that T_i equals T_o). The Gibbs free energy release of hydrogen oxidation is now smaller than the corresponding decrease in availability; there is then less *direct* energy conversion within an ideal fuel cell operating at higher temperature. For this reason, it is commonly perceived that higher temperature cells are thermodynamically inferior to lower temperature cells. Based on Eq. (3), if identical fuel and oxidizer are supplied to a fuel cell, the maximum work is dependent on cell temperature. Again the erroneous presumption that reversible work, and thus efficiency, are path dependent is concluded. This highlights the flaw of the ideal fuel cell efficiency stated in Eq. (3).

Based on its numerator, the formulation of Eq. (3) assumes the quality of heat rejected from the fuel cell (see Fig. 2) is zero. This was somewhat justifiable for pioneering fuel cells that operated nearer atmospheric temperature. Part of the work potential produced by high temperature fuel cells, however, is within the byproduct heat and not just the direct current electricity generated [10].

$$\dot{W}_{\text{potential, Heat}} = \left(1 - \frac{T_o}{T_{\text{cell}}}\right)\dot{Q}_{\text{rejected}} \qquad (5)$$

Placing this term in the numerator of the reversible fuel cell efficiency parameter is correct, since any forms of work potential are equivalent. *The maximum power produced by a high temperature cell thus requires a reversible heat engine be added for conversion of the thermal work potential.* This in no way violates the earlier comparison of the productivity of an ideal (high temperature) fuel cell and an externally reversible heat engine. *Cyclical add-ons*, such as reversible heat engines, may be considered in the determination of maximum work producible by a system [11]. This is shown in Fig. 3.

High temperature fuel cells are already attractive as topping units for heat engines [9]. The high quality heat rejected
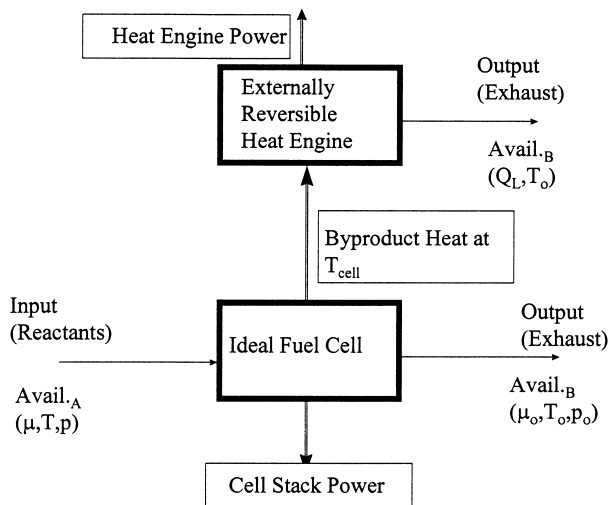
from them can help drive the bottoming cycle. An ideal fuel cell efficiency may then be accurately stated as follows.

$$\eta_{\text{ideal}} = \frac{-\Delta G + (1 - T_o/T_{\text{cell}})\dot{Q}_{\text{rejected}}}{-\Delta H} \qquad (6)$$

The allowance for a reversible bottoming cycle to utilize the rejected heat produces significant changes in the ideal efficiency calculations of high temperature cells. Consider a solid oxide fuel cell and molten carbonate cell which electrochemically oxidize hydrogen at 1000°C and 650°C, respectively. The solid oxide fuel cell's ideal efficiency increases 31%, from 0.71 to 0.93. The molten carbonate fuel cell's ideal efficiency increases 16.25%, from 0.80 to 0.93. Notice the modified relation also results in the high temperature cells having the same efficiency as a cell at atmospheric temperature (i.e. $\eta_{\text{cell}} = 0.93$). *The modified relation thus proves higher temperature fuel cells are not thermodynamically inferior to lower temperature cells as commonly perceived. Their equivalence is, however, based upon the incorporation of a reversible heat engine.* The numerator of Eq. (6) is the true representation of maximum work.

4. Conclusions/recommendations

High temperature fuel cells are becoming desirable alternatives for power generation. Fuel cell efficiencies are not limited by temperature considerations as heat engines are, but the 'non-Carnot limited' label should not imply a presumed superiority of fuel cells in contrast to externally reversible heat engines. Both energy converters conserve the exergy supplied to them and, thus, neither one has *better* performance than the other. The actual comparison should be between a fuel cell *system* and a heat engine *system*. The combustion irreversibility in the latter is the primary cause of its poorer performance.

Ideal fuel cell efficiency, as conventionally stated, does not allow for consideration of the quality of heat rejected by the fuel cell. It is thus an incomplete measure of the work potential of a high temperature fuel cell. An appropriate new expression has thus been developed, which also disproves the stated inferiority of high temperature cells in comparison to their lower temperature counterparts. Note the developments are primarily theoretical reconsiderations of idealized devices in which no irreversibilities are present.

Fig. 3. Arrangement for realization of maximum power from a high temperature fuel cell system.

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