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DETAILED ANALYSIS OF AN ENDOREVERSIBLE FUEL CELL : MAXIMUM POWER AND OPTIMAL OPERATING TEMPERATURE DETERMINATION

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ABSTRACT

Producing electrical work in consuming chemical energy, the fuel cell (FC) is forced by the 2nd law to reject heat to its surrounding. However, as it occurs for any other type of engine, this thermal energy cannot be exchanged in an isothermal way in finite time or through finite areas. As it was already done for various types of systems, including chemical engines, the fuel cell is here studied within the finite time thermodynamics framework. An endoreversible fuel cell is then defined, internally reversible but producing entropy during heat exchanges with its ambience. Considering usual H₂/O₂ and H₂/air chemical reactions and two different types of heat transfer laws, an optimal value of the operating temperature is highlighted, that corresponds to a potentially maximum produced electrical power. Finally, two fundamentals results are obtained : high-temperature fuel cells could extract more useful power from the same quantity of fuel than low temperature ones, but with lower efficiencies ; thermal radiative exchanges between the fuel cell and its surrounding have to be avoided so far as possible, because of their negative effects on optimal operating temperature value. These results emphasized the importance of heat management system of such energy converters, not only for its durability but also for its performances.

Keywords: Fuel cell, efficiency, finite time thermodynamics, entropy, endoreversibility.

1. INTRODUCTION

The fuel cell (FC) is usually described as a system that directly converts into electricity the chemical energy provided by an isothermal electro-chemical process, based for example on the hydrogen/oxygen couple as fuel and combustive ; Larminie and Dicks (2003). Trying to convert into work the chemical energy carried by reactants, such system could be also viewed as a particular type of engine.

Thereby, as any other engine and according to the second law of thermodynamics, all provided chemical energy could not be converted into work and a heat quantity is always rejected by the FC to its surrounding. As demonstrated by Wright (2004) and later by Vaudrey *et al.* (2008), the minimum thermal energy released, corresponding to the maximum produced work, is rejected by a *reversible fuel cell* (RFC), i.e. with no internal production of entropy. In order to include the FC into the finite time thermodynamics framework, equivalence between the RFC and the *Carnot heat engine* (CHE) is demonstrated in the present study.

This result leads to a new definition of the *endoreversible fuel cell* (EFC) and could result in the proposal of more realistic bounds and then performances criteria for FC systems. It also emphasize the strong influence of the temperature difference between FC and its ambience, and consequently of the thermal management system, on its performances.

2. FINITE TIME THERMODYNAMICS

As it was highlighted by Chambadal (1957) and Novikov (1958) and later by Curzon and Ahlborn (1975), a reversible (Carnot) heat engine i.e. that have the highest thermal efficiency, can only operate in exchanging heat in an infinitely slow manner. No notable work quantity could then be produced in a limited duration process. Actually, such ideal converter cannot produce any useful power.

Indeed, energy or mass transfers during finite durations or across finite areas need the existence of drops in intensive physical parameters, like e.g. temperature or chemical potential. Fourier or Fick laws are the most simple examples of such relationships between *flux* (heat transfer rate or mass flow) and *forces* (temperature difference or chemical potential difference). Any difference in intensive parameters always leads to a production of entropy, and consequently to a decrease of whole system performances, Bejan (1997). Production of any rate of work could hence not be done without a relative lost of efficiency, regarding to the Carnot's one, due to entropy production in exchange processes.

Taking into account these external irreversibilities in the analysis and optimization of system performances is the scope of the *finite time thermodynamics*, Bejan (1997); Wu *et al.* (1999); Chen and Sun (2004); Sieniutycz and Jezowski (2009). This approach allow to formulate more

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realistic performance criteria, regarding to operating conditions of actual systems.

A system internally reversible i.e. producing entropy only because of irreversible exchange processes with its surrounding, is usually qualified as *endoreversible*. The concept of *endoreversibility*, originally proposed by Rubin (1979), has been successfully applied to a large scale of systems, including different types of engines, heat pumps or distillation devices. When a system is qualified as *irreversible*, it means that it houses both internal and external entropy productions.

3. FUEL CELLS AND CHEMICAL ENGINES

Finite time thermodynamics have been previously applied to the study of chemical engines and fuel cell (FC) models. A Carnot heat engine fed by an exothermic chemical process in a flow reactor was studied by Ondrechen *et al.* (1980b). Authors analyzed the influence of limited dwell time and rate of reaction on the produced mechanical power. For different orders of reaction, they highlighted the existence of maximum resulting mechanical power reactants feeding rates. Later, they extended the same idea to temperature dependant reaction rates phenomena, Ondrechen *et al.* (1980a). De Vos (1991) considered the same type of system but in a slightly different way. He proposed to extend to matter the heat resistance and reservoir concepts of the Curzon and Ahlborn heat engine (CAHE). Whereas efficiency of the CAHE is limited by the rate at which heat can be transferred from the working fluid to heat reservoirs, the one of a chemical engine is similarly limited by the rate at which matter can be transferred from chemical reactants flow to reaction sites. Temperature difference between heat reservoirs in the CAHE is then replaced by a chemical potential difference. The author analyzed the impact of both temperature and chemical potential differences on the energy converter optimal performances, but with linear mass transfer laws. The simpler case of an isothermal chemical engine, i.e. with only a chemical potential difference, fed by linear mass transfer laws have been analyzed by Chen *et al.* (1997b). As some authors did for heat transfer laws, De Vos (1985), other types of mass transfer laws have later been tested by Gordon (1993) and Gordon and Orlov (1993) for an isothermal chemical engine. Later, the effect of a possible *mass leak* within the system was considered by Chen *et al.* (1998).

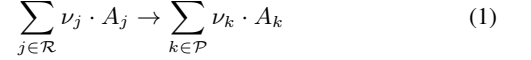
The specific case of FC, including electrochemical phenomena, was treated more lately by Sieniutycz (2010, 2011). Author introduced *electrochemical potentials* (instead of chemical ones) and *overpotential phenomenon* in a model similar to the one of De Vos (1991) previously quoted. Unfortunately, the interesting formalism proposed in this studies have not been applied to practical case of FC systems, including for example an hydrogen/oxygen reaction, or the typical operating temperature range of a specific FC technology.

More complex FC system configurations, including combined cycles with heat engines, have been studied by Chen *et al.* (1997a); Zhao and Chen (2009); Zhang and Chen (2010, 2011). However, in all these studies, FC is always considered only as a system producing both electricity and heat, the latter being used to feed classical endoreversible heat engines. Finite time thermodynamics is then applied only to the combined cycle heat engine and not to the fuel cell.

Some other FC particular topics were also concerned by a finite time thermodynamical analysis, like current path within the feeding ducts in Watowich and Berry (1986); Vargas and Bejan (2004) or design of the thermal management system in Sharifian and Saidi (2005). Nevertheless, none of these previous studies took into account neither a particular and practical chemical reaction used in real fuel cells nor the specific parameter ranges of different FC technologies, like e.g. high or low temperature systems.

4. REVERSIBLE FUEL CELL AND CARNOT HEAT ENGINE

Let us consider an open and steady state system, similar to a fuel cell i.e. operating at constant temperature T and pressure p and housing the followed exothermic chemical reaction :



with A_i the chemical species and ν_i their corresponding stoichiometric coefficients. \mathcal{R} and \mathcal{P} are respectively the groups of reactants and products of previous reaction, both considered as ideal gases. Besides molar quantities of reactants and products, it is assumed that the whole system exchanges work W_1 and heat Q_1 with its surrounding. Considered

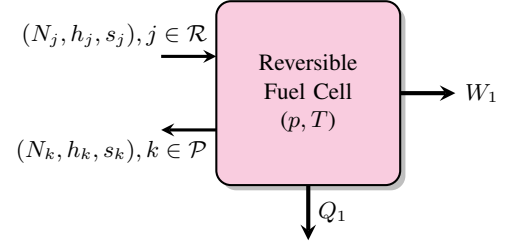


Fig. 1 Schematic diagram of system 1 : an isothermal and isobaric open system operating in steady state at pressure p and temperature T , producing work W_1 and heat Q_1 while consuming chemical reactants N_j and rejecting chemical products N_k .

system is drawn on Fig. 1 and noted 1 in the rest. It directly converts into work the chemical energy provided by reaction (1). Its energy and entropy balances are respectively :

$$\delta W_1 = -\Delta h(T) \cdot d\xi - \delta Q_1 \quad (2)$$

$$\delta_i S_1 = \Delta s(\mathbf{p}, T) \cdot d\xi + \frac{\delta Q_1}{T} \quad (3)$$

with Δh and Δs the variations of molar enthalpy and molar entropy through reaction (1), δQ_1 the exchanged heat quantity, $\delta_i S_1$ the internal production of entropy, \mathbf{p} the vector of the partial pressures of both reactants and products and ξ the reaction progress coordinate defined by :

$$d\xi = \left(-\frac{dN_j}{\nu_j} \right)_{j \in \mathcal{R}} = \left(\frac{dN_k}{\nu_k} \right)_{k \in \mathcal{P}} \quad (4)$$

Combining (2) and (3), the variation of produced work can be expressed as :

$$\delta W_1 = -\Delta g(\mathbf{p}, T) \cdot d\xi - T \cdot \delta_i S_1 \quad (5)$$

with Δg the variation of the Gibbs energy g for chemical process (1). Logically, the maximum value of work δW_1 will be produced by a reversible system, i.e. with no internal production of entropy ($\delta_i S_1 = 0$) :

$$\delta W_{1,\max} = \delta W_{1,\max} = \delta W_{1,\text{rev}} = -\Delta g(\mathbf{p}, T) \cdot d\xi \quad (6)$$

Dividing this provided work by the reaction progress results on the molar reversible work w_{rev} in J/mol, defined as :

$$w_{1,\text{rev}} = \frac{\delta W_{1,\text{rev}}}{d\xi} = -\Delta g(\mathbf{p}, T) \quad (7)$$

that corresponds to the quantity of useful energy provided by reversible system 1 for one mole of consumed chemical reactants. The energy efficiency η will be defined as the fraction of useful energy w_1 on consumed energy. For the considered reversible system, Larminie and Dicks (2003) :

$$\eta_{1,\text{rev}} = \frac{w_1}{-\Delta h(T)} = \frac{\Delta g(\mathbf{p}, T)}{\Delta h(T)} \quad (8)$$

Regarding to a real FC, the RFC would be characterised by the absence of overpotentials which are direct results of internal production of entropy,

Zhao *et al.* (2008). The well known polarization curve i.e. the voltage vs. current produced by the FC should then be replaced by a constant value of voltage E in V , equal to the “reversible” one, Larminie and Dicks (2003) :

$$E_{\text{rev}} = -\frac{\Delta g(\mathbf{p}, T)}{n_e \cdot F} \quad (9)$$

F is the Faraday constant and n_e the number of electrons exchanged by each molecule of fuel (2 in the hydrogen/oxygen reaction (21)). Examples of such curves are drawn on Fig. 2.

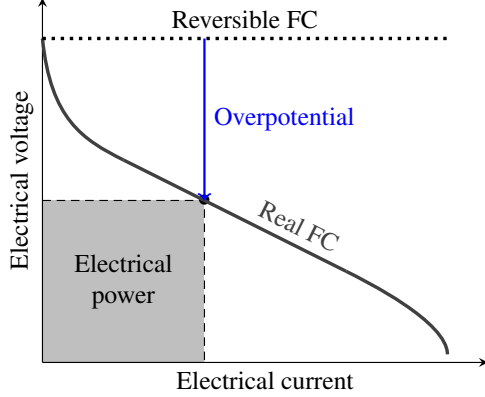


Fig. 2 Schematic polarization curve (voltage vs. current) of a real and a reversible fuel cell (RFC). Contrary to the real one, the RFC have an electrical potential E independent on the current value. E only depends on both operating temperature and partial pressures of chemical reactants and products, as highlighted by relation (9).

Let us consider now an other system, noted 2 and drawn on Fig. 3, that produces only heat from the same chemical reaction (1), and used as a hot source of a Carnot heat engine (CHE). First and second laws applied to this combustion system gives :

$$0 = -\Delta h(T) \cdot d\xi - \delta Q_2 \quad (10)$$

$$\delta_i S_2 = \Delta s(\mathbf{p}, T) \cdot d\xi + \frac{\delta Q_2}{T^*} \quad (11)$$

with T^* the corresponding temperature of chemical process. Supposing it reversible ($\delta_i S_2 = 0$) and combining (10) and (11), the theoretical temperature T^* arises, sometimes called *entropic temperature* as by Laouir *et al.* (2001) or *equilibrium temperature* by De Groot (2004) :

$$T^*(\mathbf{p}, T) = \frac{\Delta h(T)}{\Delta s(\mathbf{p}, T)} \quad (12)$$

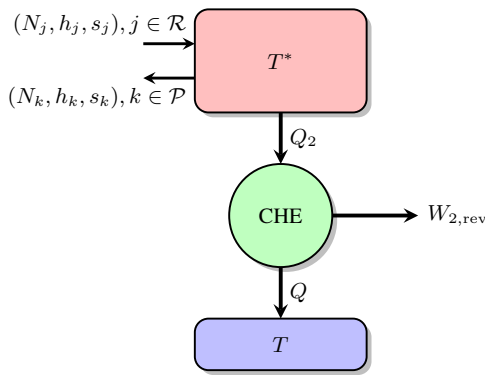


Fig. 3 Schematic diagram of system 2 : a flow reactor housing the same exothermic chemical process as system 1 (Fig. 1) but occurring at equilibrium temperature T^* and producing only heat quantity Q_2 . Reactor is used as heat source of a Carnot heat engine (CHE) that produces work $W_{2,\text{rev}}$ and rejecting heat Q to heat sink at temperature T .

As explained by Lutz *et al.* (2002); Ro and Sohn (2007), this idealized temperature corresponds to the one reached by a combustion process as (1) that both consumes and rejects reactants and products at temperature T . It is very important to notice the difference between *equilibrium temperature* T^* and the usual *adiabatic flame temperature* T_{ad} . The latter is the temperature reached by an adiabatic combustion process, i.e. if the whole enthalpy variation is used to heat up the reaction, see Bejan (1997). At the contrary, combustion phenomenon in system 2 is not adiabatic, it continuously exchanges heat of reaction with combined heat engine. Temperature T^* is reached in using heat contained in chemical products and rejected during their cooling from T^* to T , to heat up reactants from T to T^* .

A Carnot heat engine (CHE) operating between temperatures T and T^* in consuming heat δQ_2 , provided by previous ideal combustion system, can produce a work quantity Wright (2004); Vaudrey *et al.* (2008) :

$$\begin{aligned} \delta W_{2,\text{rev}} &= \delta Q_2 \cdot \eta_2 = \delta Q_2 \cdot \left(1 - \frac{T}{T^*(\mathbf{p}, T)}\right) \\ &= \underbrace{-\Delta h(T)}_{=q^*} \cdot d\xi \cdot \left(1 - \frac{T \cdot \Delta s(\mathbf{p}, T)}{\Delta h(T)}\right) \\ &= -\Delta g(\mathbf{p}, T) \cdot d\xi \end{aligned} \quad (13)$$

It can be seen that in relations (6) and (13) that $w_{1,\text{rev}} = w_{2,\text{rev}}$. Consequently, $\eta_{1,\text{rev}} = \eta_{2,\text{rev}}$. This leads to conclude on the thermodynamical equivalence of both reversible systems, i.e. of RFC and CHE. Indeed, system 2 is defined as a burner (housing an exothermic chemical reaction) associated to a Carnot engine that producing work. Efficiency η_2 of the whole system is the one of a classical ideal heat engine. It is important here to notice that temperature T^* is not really considered as an actual physical temperature but more as a mathematical way to express a chemical engine efficiency in the same form $1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}$ as for heat engine, as highlighted by Eq.(13).

Hence, a reversible fuel cell could be considered as a Carnot heat engine operating with a heat source at equilibrium temperature T^* and a cold sink at its own temperature T (see Fig. 3).

5. ENDOREVERSIBLE FUEL CELL

As originally demonstrated by Chambadal (1957) and Novikov (1958), an entirely reversible engine can exchange thermal energies only in infinitely slowly processes and finally can not produce any useful power. Heat transfer can not occur across finite exchange areas in an isothermal way and a finite difference of temperature is necessary to allow rejection of produced heat. On Fig. 4, the FC operates at temperature T in an ambience at the cold temperature noted $T_c < T$. Difference $T - T_c$ between the FC operating temperature and the surrounding one vary with the specific FC technology. It is weak for low temperature systems like PEMFC and could be very important for high temperature systems such as SOFC.

Rejected molar heat quantity $q = \delta Q/d\xi$ in J/mol is now a function of temperatures T and T_c , see Fig. 4. De Vos (1985) showed that different heat transfer laws could be applied to this system. Present study will consider the general heat transfer law as :

$$q(T, T_c) = k_n \cdot (T^n - T_c^n) \quad (14)$$

where k is equivalent to a thermal conductance (usually defined as a product of heat transfer coefficient and heat transfer area), but divided by reaction progress as previously did for molar work of Eq.(7) and lately for molar heat rejected q . n is an integer representative of the type of heat transfer law. Then, the heat exchange process will be called linear as with usual thermal convection if $n = 1$, and nonlinear if $n > 1$.

The equivalent heat engine of Fig. 4 operating between T and T^* and being internally reversible (i.e. endoreversible), its molar entropy balance is :

$$\frac{q^*(T)}{T^*(\mathbf{p}, T)} = \frac{q(T, T_c)}{T} \quad (15)$$

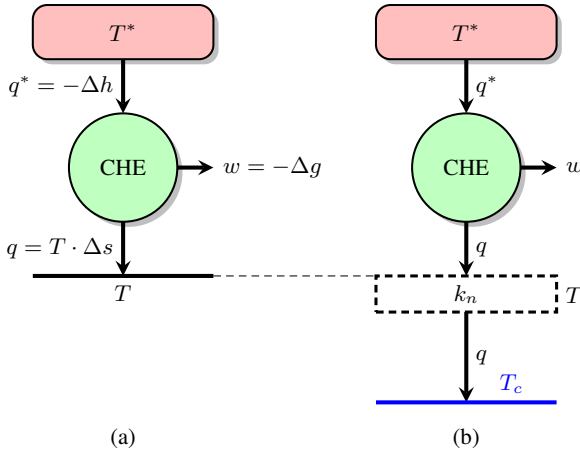


Fig. 4 Equivalent heat engines of (a) reversible fuel cell (RFC) and (b) endoreversible fuel cells (EFC).

with $q^*(T) = -\Delta h(T)$ the heat delivered by an equivalent hot heat source (Fig. 3). Combining (13), (14) and (15), the molar work becomes :

$$\begin{aligned} w &= q^*(T) \cdot \left(1 - \frac{T}{T^*(\mathbf{p}, T)}\right) = q(T, T_c) \cdot \left(\frac{T^*(\mathbf{p}, T)}{T} - 1\right) \\ &= k_n \cdot (T^n - T_c^n) \cdot \left(\frac{T^*(\mathbf{p}, T)}{T} - 1\right) \end{aligned} \quad (16)$$

and explicitly depends on temperatures T and T_c . Otherwise, related energy efficiency is :

$$\eta = \frac{w}{q^*} = 1 - \frac{T}{T^*(\mathbf{p}, T)} = \eta_{1, \text{rev}} \quad (17)$$

Let us now suppose that operating temperature T could vary from the environment one T_c to T^* . Considering expression (16) of the molar work w , three cases have to be considered :

1. If $T = T_c$, according to equation (14), no heat quantity can be exchanged and then $q = T \cdot \Delta s = 0$ (see Fig. 4). Therefore, molar variation of entropy Δs is null and chemical process can not occur. The whole system can not produce any useful work and $w = 0$.
2. If T increases, it can reach its maximum value, noted T_{\max} , that corresponds to an equality between the operating temperature and the entropic one, i.e. root of the following function :

$$f(T) = T - T^*(\mathbf{p}, T) = 0 \Rightarrow T_{\max} \quad (18)$$

This situation leads to the vanishing of Gibbs energy variation :

$$-\Delta g(\mathbf{p}, T_{\max}) = 0 \quad (19)$$

and to $w = 0$, according to (7).

3. If $T_c < T < T_{\max}$, the work w is a continuous and positive function of T which could be maximized.

Unlike other endoreversible engines, that are usually supposed to operate with independent values of hot and cold temperatures, Eq.(16) (i.e. the molar produced work) depicts a non linear link between entropic and operating temperatures, T^* and T . This situation corresponds to an equivalent heat engine whose value of the hot source temperature is a function of the cold sink one. Consequently, the maximum power corresponding temperature could not be given as the usual geometric mean of high and low temperatures $\sqrt{T_c \cdot T_{\max}}$, see Bejan (1996). The optimal temperature \hat{T} corresponds to a maximum value of w :

$$\hat{T} = \arg \max (w(T)) \quad (20)$$

This relationship will be optimized by a Newton numerical algorithm using $\sqrt{T_c \cdot T_{\max}}$ as an initial point which turns out to be a satisfying approximation (see Fig. 7).

6. HYDROGEN FUEL CELL

As a practical example, let us consider the case of an endoreversible fuel cell (EFC) operating in consuming hydrogen as fuel. Chemical reaction (1) is :



The surrounding temperature is fixed for example at $T_c = 298, 15 \text{ K}$. Thanks to experimental correlations published by Chase (2000), evolu-

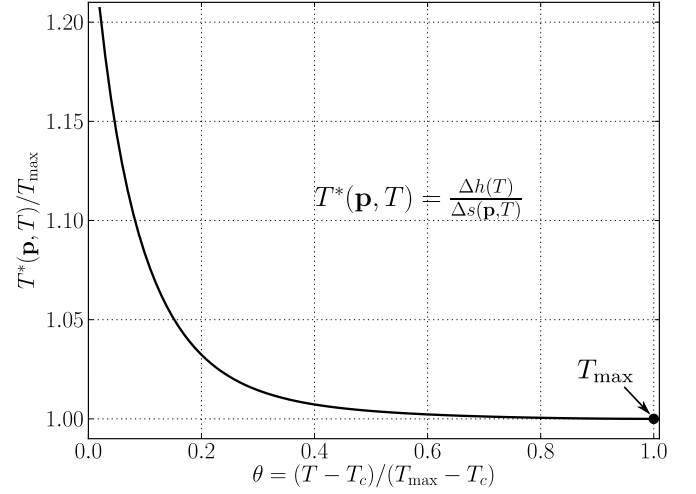


Fig. 5 Entropic temperature T^* of Eq.(12) regarding to the fuel cell (FC) operating one T for pure O_2 as combustible ($x_{\text{O}_2} = 1$). T_{\max} is the maximum value of operating temperature T and is reached when $T = T^*(\mathbf{p}, T)$.

tion of the entropic temperature T^* vs. reduced temperature θ for pure oxygen as combustible have been represented on Fig. 5:

$$\theta = \frac{T - T_c}{T_{\max} - T_c} \quad (22)$$

Dot at the end of curve represents the maximum temperature, corresponding to $\theta = 1 \Rightarrow T^* = T = T_{\max}$. Maximum temperature for pure O_2 is $T_{\max}(x_{\text{O}_2} = 1) \simeq 4310 \text{ K}$. Using air as combustible leads to a similar curve, but with $T_{\max}(x_{\text{O}_2} = 0, 21) \simeq 3884 \text{ K}$.

Using Eqs.(8) and (17), respective energy efficiencies for pure oxygen and air as combustible are represented on Fig. 6, with values of coordinate θ based on maximum temperature with pure oxygen $T_{\max}(x_{\text{O}_2} = 1)$. It can be observed on Fig. 6 a quasi linear decrease of η with the operating temperature T , leading to a zero value for $T = T_{\max}$ (see relation (19)). Energy efficiency corresponding to air consumption reach zero at its own value of T_{\max} , less than the one of pure oxygen, as presented on the right part of figure 6.

Range of θ values does not start at zero because of the possible liquid water formation that can occur below 100°C . Hence, below this temperature, it is extremely difficult to know whether the produced water is in liquid or vapor phase. Values of enthalpy variation Δh and then of energy efficiency (8) being strongly different if water is in gaseous or liquid phase, this specific temperature range have not been treated.

6.1. Linear heat transfer law

Considering the molar work (16) produced with linear transfer law ($n = 1$) as for example with a heat convection phenomenon, it can be given by :

$$w = k_1 \cdot (T^*(\mathbf{p}, T) - T) \cdot \left(1 - \frac{T_c}{T}\right) \quad (23)$$

Expression (23) incidentally corresponds to the work produced by a Carnot heat engine (CHE) operating between temperatures T_c and T and consuming some molar heat $q = k_1 \cdot (T^*(\mathbf{p}, T) - T)$. Numerical results

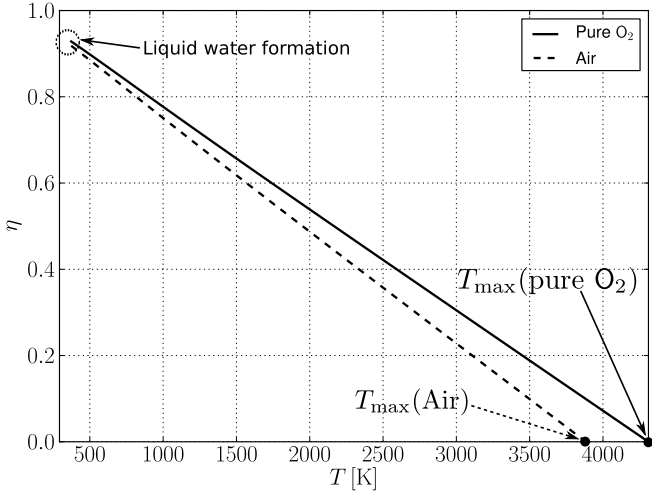


Fig. 6 Energy efficiencies η of RFC (Eqs.(8) and (17)) fed by pure O_2 (full line) and air (dashed line) as combustive. η vanish in both cases for respective values of T_{\max} .

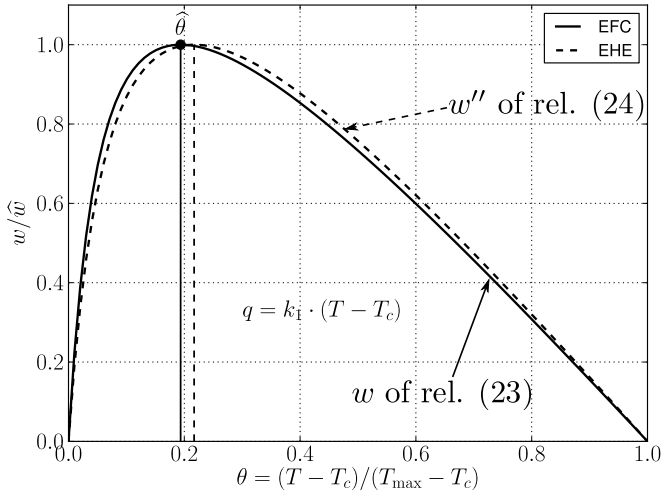


Fig. 7 Reduced molar work w/\hat{w} vs. θ with the finite conductance (14) for RFC and for an endoreversible heat engine (EHE) operating between constants temperatures T_c and T_{\max} .

are drawn on Fig. 7. Evolution of reduced work w/\hat{w} vs. reduced operating temperature θ of Eq.(22) is drawn in continuous line (curve 1). \hat{w} is the maximum value of w regarding to temperature T . The second dashed line (curve 2), corresponds to the case where hot temperature is supposed to be constant and equal to the highest operating one T_{\max} and where expression of the molar work w'' corresponds to those of an usual endoreversible heat engine (EHE) :

$$w'' = k_1 \cdot (T_{\max} - T) \cdot \left(1 - \frac{T_c}{T}\right) \quad (24)$$

In fact, this engine is the one represented on Fig. 4b, but in replacing variable high temperature T^* by the constant one T_{\max} . In this particular case, it is easy to show that, Chambadal (1957) :

$$\frac{\partial w''}{\partial T} = k_1 \cdot \left(\frac{T_c \cdot T_{\max}}{T^2} - 1\right) = 0 \Rightarrow \hat{T} = \sqrt{T_c \cdot T_{\max}} \quad (25)$$

and the optimal operating temperature \hat{T} also leads to a maximum work :

$$\hat{w} = k_1 \cdot \left(\sqrt{T_{\max}} - \sqrt{T_c}\right)^2 \quad (26)$$

and to the famous form related energy efficiency :

$$\hat{\eta} = 1 - \frac{\hat{T}}{T_{\max}} = 1 - \sqrt{\frac{T_c}{T_{\max}}} \quad (27)$$

$\hat{\eta}$ is the energy efficiency of EHE operating between T_c and T_{\max} when produced work is maximum. Difference between curves 1 and 2 is a direct consequence of nonlinear link between the entropic temperature T^* and the operating one T , see relation (12). Therefore, the value of the optimal temperature \hat{T} corresponding to $w = \hat{w}$ is slightly modified and actually different from those obtained by a geometric mean (25) of both high and low temperatures. Main results are presented in Table 1 for an hydrogen/air chemical reaction.

Table 1 Maximum power operating temperature \hat{T} and related energy efficiency $\hat{\eta}$ for variable and constant equivalent high temperatures. Concerned chemical process involve air as combustive.

High temperature	$T^*(p, T)$	T_{\max}
\hat{T}	992 K	1076 K
$\hat{\eta}$	75,3%	72,3%

The well used curve $w/\hat{w} = f(\eta)$ is drawn on Fig. 8 for each endoreversible system. Difference between curves, due to nonlinearity of

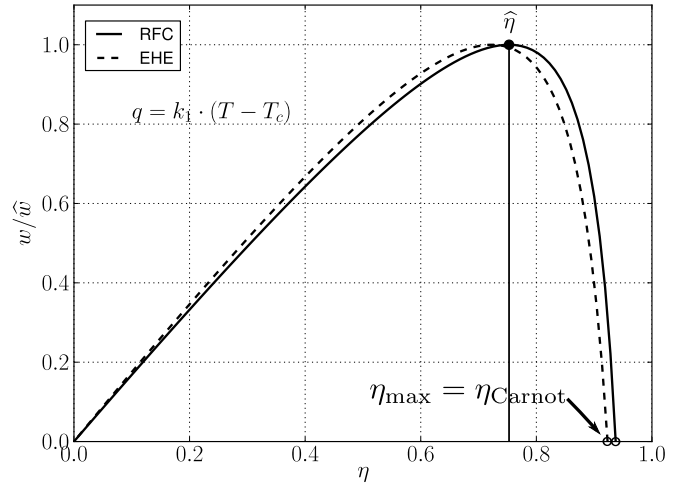


Fig. 8 Reduced molar work w/\hat{w} regarding to energy efficiency η for an EFC and for an EHE operating between T_c and T_{\max} . Maximum i.e. Carnot values of efficiencies, corresponding to thermal equilibrium between converters and ambiance ($T = T_c$) and then to no work produced, are highlighted on the right of horizontal axis.

$T^* = f(T)$ is here more significant, and leads to different values of maximum (Carnot) efficiencies, emphasized on the right part of efficiencies axis.

This first result is interesting but does not take into account the difference of heat transfer types between low and high-temperature systems. Hence, high temperature heat transfer processes are often driven by radiative effects.

6.2. Nonlinear heat transfer law

Let us consider now the case of a pure radiative heat transfer phenomenon ($n = 4$) between the FC and the surrounding. This simple configuration is different from the one of a real high temperature FC, that often exchange heat by both convection and radiation, but is useful to understand

the specific effect of radiative exchange on performances. Produced molar work can be expressed as :

$$w = k_4 \cdot (T^4 - T_c^4) \cdot \left(\frac{T^*(\mathbf{p}, T)}{T} - 1 \right) \quad (28)$$

As presented on Fig. 9 (full line), the nonlinear heat exchange law leads to a strong increase of the optimal temperature : $\hat{T} \simeq 2910$ K in the same chemical conditions as previously. This result could be explained by the

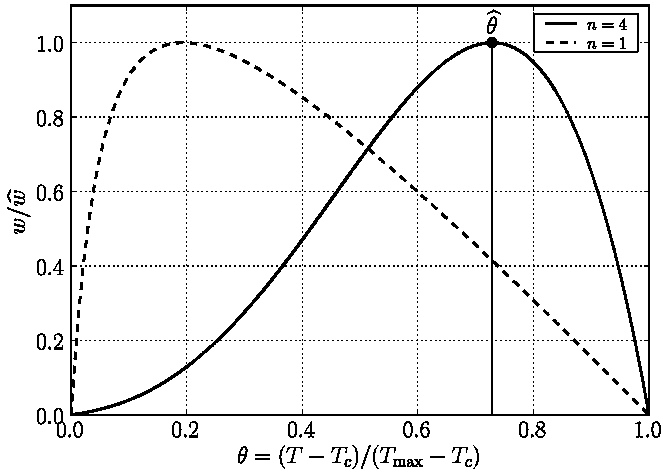


Fig. 9 Evolutions of reduced molar work w/\hat{w} vs. θ for $n = 4$ (continuous curve) and $n = 1$ (dashed curve).

fact that the same heat quantity needs a higher value of the temperature difference to be exchanged by a radiative way than thanks to convective phenomenon. The molar heat q corresponding to a maximum produced work could be only released beyond a temperature difference higher with radiative exchange than with only a convective one. To make the difference with previous linear case, we have drawn on the same graph the molar work corresponding to the linear heat transfer law (dashed line).

Efficiency-work curves of both linear and nonlinear heat transfer laws are presented on Fig. 10. Simultaneously to the increase of the max-

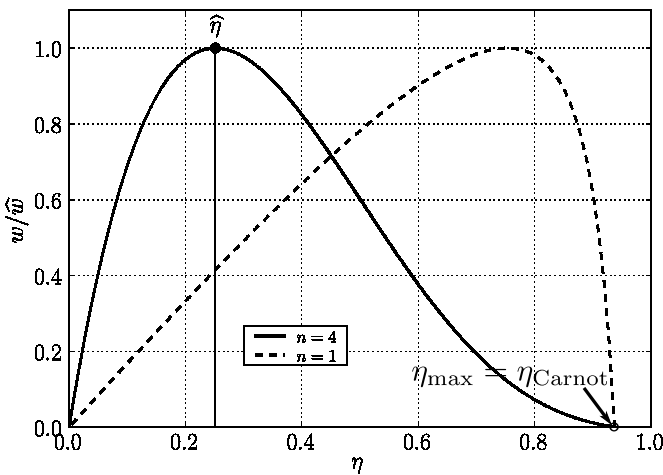


Fig. 10 Evolutions of reduced molar work w/\hat{w} regarding to energy efficiency η with $n = 4$ (full line) and $n = 1$ (dashed line). For any type of heat transfer law, minimum operating temperature $T = T_c$ corresponds to maximum efficiency $\eta = \eta_{\max}$ and to $w = 0$.

imum work operating temperature, it appears a strong decrease of related

energy efficiency : $\hat{\eta} \simeq 25\%$. As presented on Fig. 9, an increase of the operating temperature corresponds to a decrease of its efficiency. Hence, the radiative heat transfer process appears to be unfavourable regarding to EFC performances because it moves up the optimal operating temperature from those corresponding to convective heat exchange phenomena. Finally, a relevant thermal management system design for high temperature FC will have to minimize radiative losses effects in order to decrease as much as possible the corresponding optimal temperature. The closer it is from operating temperature and the better are potential performances of the system.

6.3. Consequences on different fuel cell technologies

Previous curves are useful for making the difference between low and high-temperatures fuel cells. Typical range of operating temperatures of protons exchange membrane fuel cells (PEMFC), i.e. $60^\circ\text{C} \leq T \leq 120^\circ\text{C}$ is drawn on the left of figure 11. As previously presented on

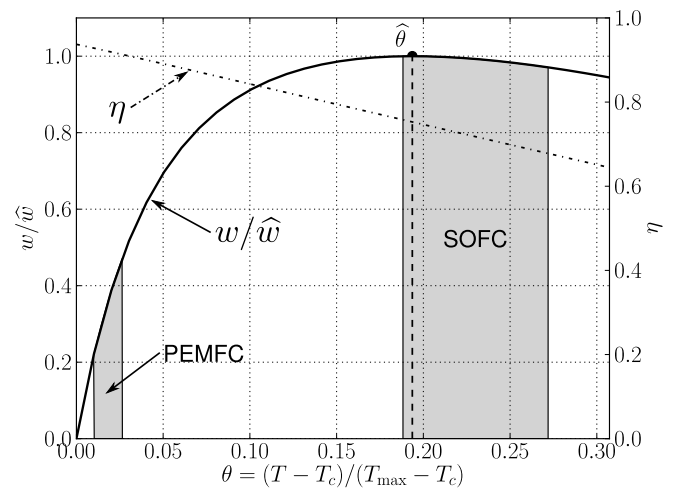


Fig. 11 Reduced molar work and efficiency of different types of FC for air as combustive. Low temperature FC as e.g. PEM are characterized by high values of energy efficiency η but low values of produced work w . At the contrary for high temperature FC as e.g. SOFC, produced work is potentially high but balanced by a lower efficiency.

Fig. 6, a low temperature hydrogen fuel cell is characterized by high value of its energy efficiency η . On a first hand, its low temperature difference with surrounding prevents to reject large heat quantity q , and according to the Carnot principle, to produce large work quantity w , as presented on Fig. 11.

On a second hand, high-temperature fuel cells, such as solid oxide ones (SOFC), can easily evacuate generated heat quantities, because of their high temperature differences with the ambience, and are also able to produce large quantities of useful work. On the right part of Fig. 11 is also drawn the typical operating temperature range of SOFC, i.e. $700^\circ\text{C} \leq T \leq 1000^\circ\text{C}$. However, this advantage is counterbalanced by a lower energy efficiency, as shown on right part of Fig. 6.

Nevertheless, operating temperature \hat{T} that corresponds to a maximum amount of work produced is even so within the temperature range of actual SOFC.

7. CONCLUSIONS

The formal equivalence between a reversible fuel cell (RFC) and a Carnot heat engine (CHE), both supplied by the same combustion process, led to describe the former within the finite time thermodynamics framework. The first result of such approach is the definition of an endoreversible fuel cell (EFC), operating in a reversible way but exchanging irreversibly heat with its surrounding, through finite thermal conductances. As for

any other type of energy converter, the finite time thermodynamics study of FC :

- provide more realistic bounds of performances, regarding to those of actual systems.
- allow to look for optimal operating conditions, corresponding for example to a maximum work produced.

Then, maximization of the produced electrical work regarding to the fuel cell operating temperature has led to highlight an optimal configuration, numerically calculated for an hydrogen/air reaction for standard conditions of pressure. If only exchanging heat with surrounding via convection process, such hydrogen fuel cell could potentially produce a maximum amount of useful power if operating at temperature $\hat{T} \simeq 992 \text{ K} = 719^\circ\text{C}$. In that case, corresponding energy efficiency is about 75%. This result is important because obtained optimal temperature is within the operating temperature range of actual solid oxide fuel cells.

However, existence of an other heat transfer process, as e.g. a radiative one, could modify the corresponding value of optimal temperature. In a pure radiative heat exchange configuration, our results show that the latter dramatically increase, far over the operating temperature range of any existing fuel cell technology. Moreover, corresponding efficiency drop to about 25%.

These results leads to conclude on the necessity for a relevant thermal management system to avoid radiative thermal effects as far as possible and to favour the convective heat exchange phenomena, for example in adapting design of heat management ancillary systems. An efficient thermal management system will be able to evacuate the heat generated while maintaining operating temperature of the FC close to the optimal one previously highlighted.

The present endoreversible fuel cell is based on an only one thermal finite conductance due to the heat transfer rate exchange with the ambience. It would be significant to also consider a non reversible chemical reaction, using for example the results of chemical thermodynamics in finite time Andresen *et al.* (1984), or a finite time electrochemistry Watowich and Berry (1986). In the same way, different types of internal entropy production could be progressively taken into account.

Moreover, design and optimization processes of fuel cell systems have also to take into account the fundamental Carnot principles. The heat rate rejected from the system to the surrounding is fundamental and strongly influences at least the electrical power produced.

NOMENCLATURE

A	chemical species
E	electrical potential (V)
F	Faraday constant (C/mol)
g	molar Gibbs energy (J/mol)
h	molar enthalpy (J/mol)
k	molar thermal conductance (J/(mol · K))
N	amount of substance (mol)
p	pressure (Pa)
\mathcal{P}	groups of products of a chemical reaction
q	molar heat (J/mol)
Q	heat or thermal energy (J)
\mathcal{R}	groups of reactants of a chemical reaction
s	molar entropy (J/(mol · K))
S	entropy (J/K)
T	temperature (K)
w	molar work (J/mol)
W	work or useful energy (J)
<i>Greek Symbols</i>	
Δ	variation of a molar quantity through a chemical reaction
η	energy efficiency
ν	stoichiometric coefficient

ξ	reaction progress (mol)
<i>Superscripts</i>	
*	equilibrium phenomenon
<i>Subscripts</i>	
c	cold temperature
i	internal production
rev	reversible phenomenon
<i>Acronyms</i>	
CAHE	Curzon and Ahlborn Heat Engine model
CHE	Carnot Heat Engine
EFC	Endoreversible Fuel Cell
FC	Fuel Cell
RFC	Reversible Fuel Cell

REFERENCES

- Andresen, B., Berry, R.S., Ondrechen, M.J., and Salamon, P., 1984, "Thermodynamics for Processes in Finite Time," *Accounts of Chemical Research*, **17**, 266–271, <http://dx.doi.org/10.1021/ar00104a001>.
- Bejan, A., 1996, "Entropy generation minimization : The new thermodynamics of finite-size devices and finite-time processes," *Journal of Applied Physics*, **79**(3), 1191–1218, <http://dx.doi.org/10.1063/1.362674>.
- Bejan, A., 1997, *Advanced Engineering Thermodynamics*, Wiley, New York.
- Chambadal, P., 1957, *Les centrales nucléaires*, A. Colin, Paris.
- Chase, M.W., 2000, *NIST-JANAF Thermochemical Tables*, American Institute of Physics.
- Chen, L., and Sun, F., 2004, *Advances in Finite Time Thermodynamics : Analysis and Optimization*, Nova Science Publishers.
- Chen, L., Sun, F., and Wu, C., 1998, "Performance of chemical engines with a mass leak," *Journal of Physics D: Applied Physics*, **31**, 1595, <http://dx.doi.org/10.1088/0022-3727/31/13/014>.
- Chen, L., Sun, F., Wu, C., and Gong, J., 1997a, "Maximum Power of a Combined-Cycle Isothermal Chemical Engine," *Applied Thermal Engineering*, **17**(7), 629–637, [http://dx.doi.org/10.1016/S1359-4311\(96\)00082-8](http://dx.doi.org/10.1016/S1359-4311(96)00082-8).
- Chen, L., Sun, F., Wu, C., and Yu, J., 1997b, "Performance characteristic of isothermal chemical engines," *Energy conversion and management*, **38**(18), 1841–1846, [http://dx.doi.org/10.1016/S0196-8904\(96\)00120-3](http://dx.doi.org/10.1016/S0196-8904(96)00120-3).
- Curzon, F.L., and Ahlborn, B., 1975, "Efficiency of a Carnot Engine at Maximum Power Output," *American Journal of Physics*, **43**, 22–24, <http://dx.doi.org/10.1119/1.10023>.
- De Groot, A., 2004, *Advanced exergy analysis of high temperature fuel cell systems*, Ph.D. thesis, Delft University of Technology, Delft, Netherlands.
- De Vos, A., 1985, "Efficiency of some heat engines at maximum-power conditions," *American Journal of Physics*, **53**(6), 570–573, <http://dx.doi.org/10.1119/1.14240>.
- De Vos, A., 1991, "Endoreversible Thermodynamics and Chemical Reactions," *Journal of Physical Chemistry*, **95**(11), 4534–4540, <http://dx.doi.org/10.1021/j100164a065>.

- Gordon, J.M., 1993, "Maximum work from isothermal chemical engines," *Journal of applied physics*, **73**(1), 8–11, <http://dx.doi.org/10.1063/1.353835>.
- Gordon, J.M., and Orlov, V.N., 1993, "Performance characteristics of endoreversible chemical engines," *Journal of applied physics*, **74**(9), 5303–5309, <http://dx.doi.org/10.1063/1.354253>.
- Laouir, A., Le Goff, P., and Hornut, J.M., 2001, "A model mechanism for assessment of exergy: analogic with the balance of a lever," *International Journal of Thermal Sciences*, **40**, 659–668, [http://dx.doi.org/10.1016/S1290-0729\(01\)01255-8](http://dx.doi.org/10.1016/S1290-0729(01)01255-8).
- Larminie, J., and Dicks, A., 2003, *Fuel Cell Systems Explained*, Wiley.
- Lutz, A.E., Larson, R.S., and Keller, J.O., 2002, "Thermodynamic comparison of fuel cells to the Carnot cycle," *International Journal of Hydrogen Energy*, **27**, 1103–1111, [http://dx.doi.org/10.1016/S0360-3199\(02\)00016-2](http://dx.doi.org/10.1016/S0360-3199(02)00016-2).
- Novikov, I.J., 1958, "The efficiency of atomic power stations," *J Nuclear Energy*, **7**(2), 125–128.
- Ondrechen, M.J., Andresen, B., and Berry, R.S., 1980a, "Thermodynamics in finite time : Processes with temperature-dependent chemical reactions," *Journal of Chemical Physics*, **73**(11), 5838–5843, <http://dx.doi.org/10.1063/1.440026>.
- Ondrechen, M.J., Berry, R.S., and Andresen, B., 1980b, "Thermodynamics in finite time : A chemically driven engine," *Journal of Chemical Physics*, **72**(9), 5118–5124, <http://dx.doi.org/10.1063/1.439744>.
- Ro, S.T., and Sohn, J.J., 2007, "Some issues on performance analysis of fuel cells in thermodynamic point of view," *Journal of Power Sources*, **167**, 295–301, <http://dx.doi.org/10.1016/j.jpowsour.2007.02.073>.
- Rubin, M.H., 1979, "Optimal configuration of a class of irreversible heat engines. I," *Physical Review A*, **19**(3), 1272–1276.
- Sharifian, L., and Saidi, M.H., 2005, "Optimization of the PEM Fuel Cell Cooling System by Entropy Generation Minimization," *3rd International Conference on Fuel Cell Science, Engineering and Technology*, ASME, Ypsilanti, Michigan, USA, <http://dx.doi.org/10.1115/FUELCELL2005-74124>.
- Sieniutycz, S., 2010, "Finite-rate thermodynamics of power production in thermal, chemical and electrochemical systems," *International Journal of Heat and Mass Transfer*, **53**(13), 2864–2876, <http://dx.doi.org/10.1016/j.ijheatmasstransfer.2010.02.009>.
- Sieniutycz, S., 2011, "Identification and selection of unconstrained controls in power systems," *International Journal of Heat and Mass Transfer*, **54**(4), 938–948, <http://dx.doi.org/10.1016/j.ijheatmasstransfer.2010.10.009>.
- Sieniutycz, S., and Jezowski, J., 2009, *Energy Optimization in Process Systems*, Elsevier.
- Vargas, J.C.V., and Bejan, A., 2004, "Thermodynamic optimization of internal structure in a fuel cell," *International Journal of Energy Research*, **28**, 319–339, <http://dx.doi.org/10.1002/er.967>.
- Vaudrey, A., Baucour, P., Lanzetta, F., and Glises, R., 2008, "Finite time analysis of an endoreversible fuel cell," *Fundamentals and Developments of Fuel Cell Conference*, Nancy, France.
- Watowich, S.J., and Berry, R.S., 1986, "Optimal Current Paths for Model Electrochemical Systems," *Journal of Physical Chemistry*, **90**, 4624–4631, <http://dx.doi.org/10.1021/j100410a031>.
- Wright, S.E., 2004, "Comparison of the theoretical performance potential of fuel cells and heat engines," *Renewable Energy*, **29**(2), 179–195, [http://dx.doi.org/10.1016/S0960-1481\(03\)00191-5](http://dx.doi.org/10.1016/S0960-1481(03)00191-5).
- Wu, C., Chen, L., and Chen, J., 1999, *Recent Advances in Finite Time Thermodynamics*, Nova Science Publishers.
- Zhang, X., and Chen, J., 2010, "Performance analysis and parametric optimum criteria of a class of irreversible fuel cell/heat engine hybrid systems," *International Journal of Hydrogen Energy*, **35**(1), 284–293, <http://dx.doi.org/10.1016/j.ijhydene.2009.09.093>.
- Zhang, X., and Chen, J., 2011, "Maximum equivalent power output and performance optimization analysis of an alkaline fuel cell/heat-driven cycle hybrid system," *Journal of Power Sources*, **196**, 10088–10093, <http://dx.doi.org/10.1016/j.jpowsour.2011.08.001>.
- Zhao, Y., and Chen, J., 2009, "Modeling and optimization of a typical fuel cell-heat engine hybrid system and its parametric design criteria," *Journal of Power Sources*, **186**, 96–103, <http://dx.doi.org/10.1016/j.jpowsour.2008.09.083>.
- Zhao, Y., Ou, C., and Chen, J., 2008, "A new analytical approach to model and evaluate the performance of a class of irreversible fuel cells," *International Journal of Hydrogen Energy*, **33**(15), 4161–4170, <http://dx.doi.org/10.1016/j.ijhydene.2008.04.062>.