Comparison between Fuel Cells and Heat Engines.

I. A Similar Approach in the Framework of Thermodynamics with Finite Speed

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The paper presents the main moments in the development of Thermodynamics with Finite Speed (TFS), the New Parameters introduced for description of Finite Speed Processes, the main formulae and tools, the main method for Speed, Temperature and other parameters of irreversible cycles optimization, called the Direct Method. We have observed that there is a similarity, between the quantitative approach of irreversible processes in Thermal Machines and those in Electrochemical Devices (Fuel Cells, Electrolysers and Batteries), based on expressing the First Law of Thermodynamics for irreversible processes with Finite Speed (combined with the Second Law) in a similar mathematical format in both fields(TM and ED). Methodologically, this is the starting point for the "unification" of TFS in the two domains developed independently: Engineering Thermodynamics and Electrochemistry.

Keywords: irreversibility, Fuel Cell, Finite Speed Thermodynamics, Direct Method

A correct comparison between Performances of Fuel Cells and Thermal Engines should be based on comparing the same kind of processes regarding their reversibility (ideal operation) or irreversibility (real operation).

This means that we have to always compare either their reversible Efficiencies, or their irreversible (real) Efficiencies. By no means can we compare reversible Efficiencies with irreversible Efficiencies, because such a "comparison" does not make any sense.

We have seen [1] already that despite of the fact that Fuel Cells do not use a thermodynamic cycle as Thermal Engines do, in order to transform a form of energy into another one (chemical energy, or heat into work), both will obey the Second Law of Thermodynamics.

In this paper we further investigate the differences and similarities of applying the Second Law for Fuel Cells and Thermal Engines, in order to compute their performances, (Efficiency and Power), using the recent achievements of Thermodynamics with Finite Speed (TFS) [10—30, 34-36, 41, 42, 44, 45, 47, 51-59]. In this relatively new approach of what we can call in general Irreversible Thermodynamics, new concepts and new equations have been introduced in order to quantitatively take into account the irreversibilities in Thermal Processes, in real Thermal Machines working with *Finite Speed*. It was shown that the main causes of irreversibilities (internal and external) depend on the same real operation parameter, which is the Finite Speed of the Piston w_p. In Fuel Cells, because the conversion of chemical energy in electricity is directly made, without using a cycle and a system of the cylinder-piston type, we cannot talk about the "speed of the piston". Because of that, it would be difficult, at first glance, "to find similarities" between the operation of real Fuel Cells and real Thermal Engines. The authors have discovered [21-23, 26, 29, 45] that despite these difficulties, very important similarities exist between the operation of real Fuel Cells and real Thermal Engines, regarding the fact that both operate with internal irreversibilities, in addition to *external* ones. Obviously, these irreversibilities decrease the performances (*Efficiency* and *Power*) in comparison with the reversible ones. In the case of Thermal Engines, along with the increase of the piston speed, these performances will decrease.

We find a very important similarity in real operating Fuel Cells. Namely, with the increase of the current density i=I/A also the performances will decrease. The very important role played by the piston speed w_p in Thermal Engines as the main cause of internal irreversibilities is played by the current density i, in all Electrochemical Devices. The real fact that any irreversible process with "Finite Speed", obeying the second part of the Second Law, will lead to a decrease of Performances (Efficiency and Power), but will also have similar equations, from a mathematical point of view. This is by no means just "a coincidence". It is based on the similar physical origins of the molecular mechanisms of generating irreversibility, when the processes take place with "finite speed". This similarity is expressed in the same mathematical format of the First Law of Thermodynamics (combined with the Second Law) for any kind of irreversible process. The expansion/compression processes in the piston - cylinder Systems (Thermal Machine) which takes place with the finite speed w_p are similar with charging/discharging of any Electrochemical Device operating with a finite density of the current i. The final result of this analogy will be reflected in the same mathematical expression of irreversible Efficiencies:

$$\eta_{irr} = \eta_{rev} \cdot \eta_{II} \qquad (1)$$

This analogy goes even further, namely the Second Law Efficiency, η_{II} has the same mathematical structure both in the case of Fuel Cells and Thermal Machines, the only difference being that in the first case *i* and in the second case w_p appears, as expected [24-26, 29, 38, 45, 47]:

$$\eta_{II} = 1 \pm \sum \frac{\text{Finite Speed of macroscopic process}}{\text{Finite Speed of microscopic process}} \qquad (2)$$

where:

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Finite Speed of macroscopic process = *i* (for Electrochemical Devices) *or* w_p (for Thermal Machines);

Finite Speed of microscopic interaction = i_o (exchange current for ED) or *c* (average molecular speed for TM);

(±) is a sign, which will be (+) for the processes in which energy is introduced in the system: charging (for ED) or compression (for TM) and (-) for processes in which energy "is produced" by the system: is obtained from the system as mechanical work, expansion for TM, or electrical work, discharge for ED.

In this way, Thermodynamics with Finite Speed (TFS) offer a "unified view" of the quantitative and qualitative approach of irreversible processes in both domains of Thermal Machines and Electrochemical Devices, based of course on First Law and Second Law of Thermodynamics, emphasizing that the origin of irreversibility in all real processes is the same, namely the Finite Speed of the processes either macroscopic or microscopic. Based on the same mathematical approach, Sensitivity Studies for Fuel Cells and Thermal Machines and Design Optimization are made in a similar way or with similar methods. In both domains the researchers and designers are looking for Optimum Speed (*i* or w_p) corresponding either to Maximum Efficiency or to Maximum Power.

The Development of *Thermodynamics with Finite Speed* and the *Direct Method*

In 1937 a German physicist M. Paul [2] studied the first Process with Finite Speed in a piston cylinder arrangement, and obtained the first equation of an adiabatically irreversible Process with Finite Speed:

$$TV^{(k-1)\cdot\left(1\pm 2.60067\cdot\frac{w}{c}\pm 3\cdot\frac{w^2}{c^2}\pm 3.6743\cdot\frac{w^3}{c^3}\right)} = Constant \qquad (3)$$

Much later (1964) and independently of this discovery, inspired from the books of W. Macke [3], A. Sommerfeld [4], and Einstein's Theory of Relativity [5, 9], S. Petrescu working for his Ph.D Thesis [11], with his adviser prof. L. Stoicescu [10] has written for the first time a new equation for the First Law of Thermodynamics for Processes with Finite Speed in closed systems (Piston - Cylinder arrangement):

$$dU = \delta Q - P_{m,i}\cdot\left(1 \pm \frac{aw}{c}\right)\cdot dV \qquad (4)$$

where *w* is the piston speed, $a = \sqrt{3k}$, $k = C_p/C_v$, $c = \sqrt{3RT_{m,i}}$

The second term in the right hand side of eq (4) is the irreversible work δW_{irr}:

$$\delta W_{irr} = P_{m,i}\cdot\left[1 \pm \frac{aw}{c}\right]\cdot dV \qquad (5)$$

This approach [10, 11] of Irreversible Processes with Finite Speed was completely new and different, in comparison with Paul's approach [2]. It seems that Paul was not interested in finding a new equation for the First Law of irreversible processes, like eq. (4), but just to get an equation of irreversible adiabatic process with Finite Speed, eq. (3).

The discovery of eq. (4), in 1964 [10, 11] could be considered the beginning of Thermodynamics with Finite Speed, because for the first time the causes for irreversibility were contained in a fundamental equation of Thermodynamics, namely in the Mathematical Expression of the First Law, written especially for irreversible processes, in an explicit way, as function of the Finite Speed of the Piston *w*, and Finite Speed of the Molecules *c*. The analogy with Einstein's Theory of Relativity [5, 9], consists in the fact that, in a way similar to the dependence of electromagnetic waves interaction on the speed of light, here, in the piston cylinder arrangement, the waves generated by the motion of the piston with finite speed *w*, depend on the average molecular speed *c*. By consequence, the piston-gas mechanical interaction, (whose measure is the irreversible elementary Work dW_{irr}) must depend on the ratio w/c. This was the seminal idea [9], which led to eq. (4) by 4 different approaches:

a) The basic kinetic-molecular model [10, 11] gave the following relationship:

$$\delta W_{irr} = P_{m,i}\cdot\left[1 \pm \frac{aw}{c} + \frac{bw^2}{c^2} \pm \ldots\right]\cdot dV = P_p\cdot dV\,; \qquad (6)$$

b) The advanced kinetic-molecular model [11, 17], based on Maxwell-Boltzmann distribution and on finite relaxation time in the system led to:

$$\delta W_{irr} = P_{m,i}\cdot\left[1 \pm 2{,}764\frac{w}{c} + 3\frac{w^2}{c^2} \pm 1{,}283\frac{w^3}{c^3} + \ldots\right]\cdot dV \qquad (7)$$

c) The phenomenological analysis based on the propagation of pressure waves, generated by the *finite speed of the piston* and the *speed of sound* in the gas [10, 11] *gave:*

$$\delta W_{irr} = P_{m,i}\cdot\left[1 \pm \frac{aw}{c}\right]\cdot dV\,; \qquad (8)$$

d) The Second Law approach [21], based on the Linear Irreversible Phenomenological Thermodynamics (LIPT) of Onsager [7] and Prigogine [8], and the concept of Entropy Generation, led to:

$$\delta W_{irr} = P_{m,i}\left[1 \pm K_1\cdot w\right]\cdot dV \qquad (9)$$

In all the above four approaches, L. Stoicescu and S. Petrescu [10, 11] have introduced something completely new in comparison with the Reversible Thermodynamics, namely the parameter $P_{m,i}$ called - instantaneous mean pressure in the system, different from the pressure on the piston P_p:

$$P_p = P_{m,i}\cdot\left(1 \pm \frac{aw}{c}\right) \qquad (10)$$

Because the two pressures are different when the *Piston Speed w* is greater than zero, and *c* smaller than infinity (infinite temperature), it was necessary to introduce two curves in the P-V diagram, thus describing such irreversible processes with Finite Speed w (fig. 1 and fig. 2).

The whole development of the Finite Speed Thermodynamics is based on eq. (4) together with all these new concepts, without which these irreversible processes cannot be described.

Irreversible cycles with Finite Speed in Thermal Machines

Based on eq. (2) and (4), L. Stoicescu and S. Petrescu have published the first study of an Irreversible Cycle with Finite Speed for the case of Otto Irreversible Cycle [11, 14]. The title of the paper [14] was essential for the Development of TFS, namely: "Thermodynamic Cycles with Finite Speed". In these papers [11, 14], an analytical expression for the Efficiency of Otto irreversible cycle with finite speed was obtained for the first time. This was the main difference between Paul's approach (studying just one irreversible process) and the fundamental approach, of "all the irreversible processes" based on the same

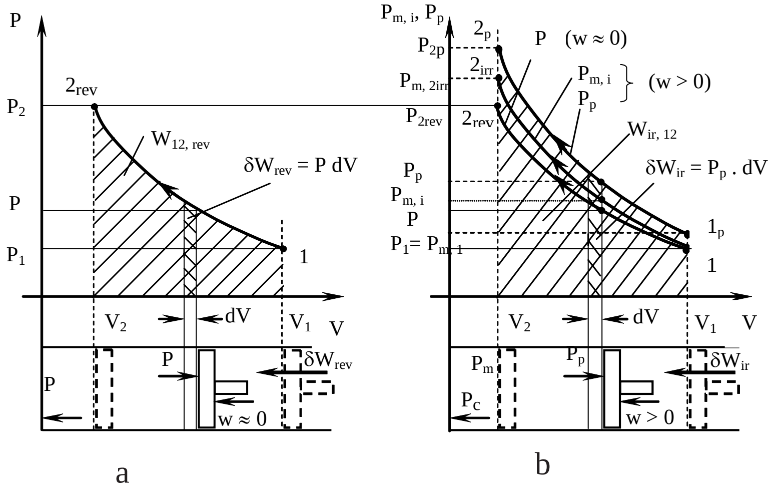

Fig. 1. Comparison between P-V diagrams for reversible **(a)** compression (w ≈ 0) and irreversible **(b)** compression (w > 0) [65]

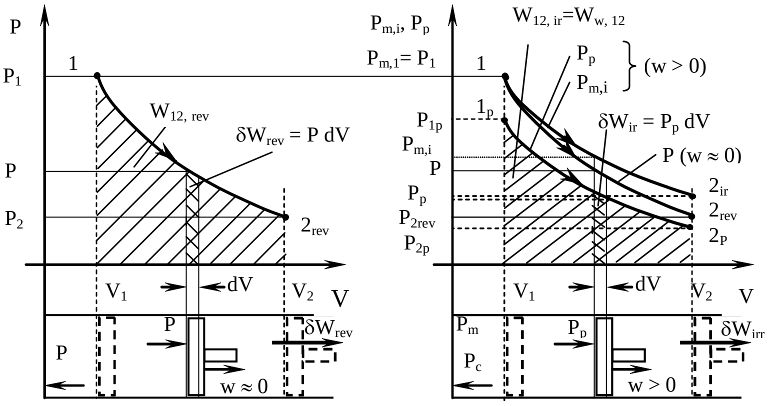

Fig. 2. Comparison between P-V diagrams for reversible (**a**) expansion (w ≈ 0) and irreversible (**b**) expansion (w > 0) [65]

Fundamental equation (4), which in fact combines the two main Laws of Thermodynamics (First and Second Laws). Building a "New Thermodynamics", namely the *Irreversible Thermodynamics for* Processes with Finite Speed (TFS) was the goal of Petrescu's Ph.D Thesis [11]. Much later, in 1992-1994, the other two causes of irreversibility, friction and throttling, were taken into account by S. Petrescu et.al. [24-26, 33]. Based on those papers [24-26] a more intensive Development of Thermodynamics with Finite Speed (TFS) led to the formulation of the Direct Method [25- 30] and its applications: [30]-[38]. It is important to remark that, from the chronological perspective, the paper [10] from TFS was published 10 years before Curtzon – Ahlborn seminal paper regarding Thermodynamics with Finite Time [29]. It is a well-known fact that this paper [29] opened the "explosive" development of the Thermodynamics with Finite Time (TFT) which did not take into account internal irrevesibilities, but only external ones, generated by temperature gradients between the System and the heat sources. The cycles studied by this early variant of TFT [29-31] were called endoreversible. This is the essential difference between the origin of TFS [10 - 20] and the origin of TFT [29]. Namely, TFS takes into account, from the very beginning, both internal and external irreversibilities, while TFT takes into account only the external irreversibilities (for endoreversible cycles).

Much later, starting with Ibrahim [36] in 1991, more and more researchers also started to take into account the internal irreversibilities in their papers on Thermodynamics with Finite Time.

A comparison between TFT and TFS approaches has been made by Petrescu et al. [37]. In TFT the accent is put on the optimization of time and temperature, usually considering only external irreversibilities. In TFS the accent is put on the optimization of the speed and temperature, but taking into account both irreversibilities (internal and external). Of course, the result of optimization will be different, and TFS gives more realistic results for Thermal Machines. TFS was Validated [38], while TFT was not yet validated in the papers where internal irreversibilities were not taken into account. Only in the last years, in papers from TFT [36] some of the internal irreversibilities were considered.

First Law of Thermodynamics combined with the Second Law for Finite Speed Processes in Electrochemical Systems: Fuel Cells, Electrolysers and Batteries.

Seminal papers regarding irreversible processes in Thermal Machines [10-20] were followed by studies of Irreversible Processes in Electrochemical Systems by V. Petrescu , S. Petrescu [21] and S. Sternberg et. al. [22, 23]. These studies resulted in the generalization of the First Law of Thermodynamics for Finite Speed Processes for Electrochemical Devices (Fuel Cells, Electrolysers and Batteries) [47, 29, 26, 45]. Lately, this led to a Unified approach of Thermal Machines and Electrochemical Devices using a unique method, the Direct Method [27], [29]. This Method is based on the fact that the First Law of Thermodynamics for Finite Speed Processes has *the same mathematical format* for both Thermal Machines and Electrochemical Devices, in the case of Irreversible Processes.

Reversible Performances in Hydrogen – Oxygen Fuel Cell

In a H_2/O_2 Fuel Cell electrical power P_e is produced by means of "controlled" chemical reactions which take place in the porous anode and cathode (fig. 3). In this Fuel Cell

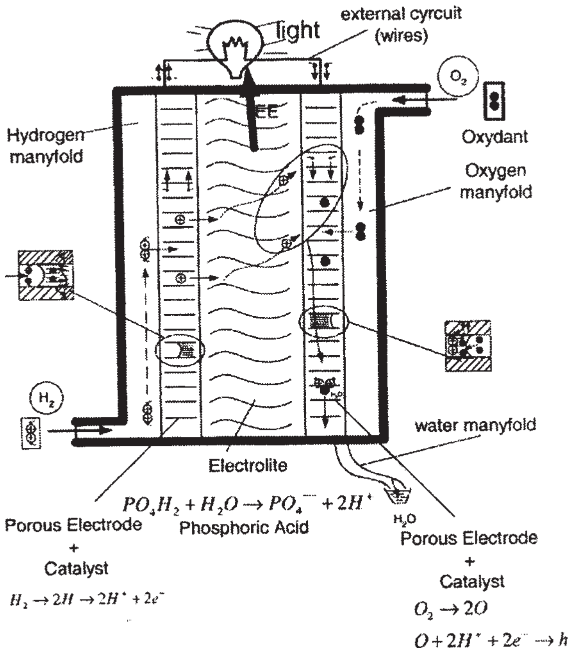

Fig 3. Hydrogen-Oxygen Fuel Cell [65]

pure Hydrogen and Oxygen are continuously added to the cell producing water and electricity.

The chemical reaction at the anode is:

$$H_2 + 2OH^- \to 2H_2O + 2e^- \tag{11}$$

and at the cathode:

$$H_2O + \frac{1}{2}O_2 + 2e^- \to 2OH^- \tag{12}$$

By the addition of equations (11) and (12), we get the full chemical reaction in the fuel cell:

$$H_2 + 2OH^- + H_2O + \frac{1}{2}O_2 + 2e^- \to 2H_2O + 2e^- + 2OH^-,\ or:$$

$$\underbrace{H_2 + \frac{1}{2}O_2}_{Reactants} \to \underbrace{H_2O}_{Product} + W_{el.} \tag{13}$$

The maximum work can be calculated from the First and Second Law of Thermodynamics for reversible processes (for electrical current I → 0), as follows:

$$(Ist) \quad dU = \delta Q_{rev} - pdV - \delta W_{el} \tag{14}$$

$$(IInd) \quad \delta Q_{rev} = TdS \tag{15}$$

With eq. (15) in (14) we get:

$$dU - TdS + pdV = -\delta W_{el} \tag{16}$$

For a reaction at constant temperature T and constant pressure p we get:

$$d(U + pV - TS) = -\delta W_{el} \tag{17}$$

Integrating this equation (7) for a finite process between states 1 and 2:

$$\int_1^2 dG = \int_1^2 -\delta W_{el} \tag{18}$$

or

$$\Delta G = -W_{el} \tag{19}$$

where: the Variation of Gibbs Free Enthalpy ΔG can be calculated from the equation:

$$\Delta G = \underbrace{\sum \Delta G^0_{f,p}}_{products} - \underbrace{\sum \Delta G^0_{f,r}}_{reactants} \tag{20}$$

here: ΔG_f^o represents the Gibbs Free Enthalpy (or Gibbs Potential) required to form the particular molecule from the elements.

By consequence, for the global fuel cell chemical reaction (13) we get:

$$\Delta G = \sum \Delta G^0_{f,H_2O} - \sum \Delta G^0_{f,H_2} - \sum \Delta G^0_{f,O_2} = \\ = -237180 - 0 - 0 = -237180\ kj/kmol \tag{21}$$

Since the molecular mass of H_2O is 18 kg/kmol, one can compute the variation of G per kg of H_2O produced:

$$\Delta G' = \frac{\Delta G}{M_{H_2O}} = -\frac{237180}{18} = -13177\frac{kJ}{kg} \tag{22}$$

Finally, from (19) we get:

$$\dot{W}_{FC\ max} = 13177\frac{kJ}{kg} \tag{23}$$

The work done to convey the electrons from the cathode to the anode is also equal to *nFV*° (Faraday Law), where *n* represents the gram-moles of electrons, *F* is the Faraday constant

$$F = 96500\, C/g \cdot mol \tag{24}$$

and V° is the electrical potential across the anode and cathode when the circuit is open, that is when the external electrical resistance R_e is disconnected. Then we have:

$$V^o = -\frac{\Delta G}{nF} \quad (Open\ Circuit\ Voltage) \tag{25}$$

Irreversible Performances of a real Fuel Cell operating with a *finite current I* and having an *internal Resistance R_i*

All the real Fuel Cells working with "finite speed", expressed by the finite electrical current intensity I, have three irreversibilities generated by three polarizations: Activation, Ohmic and Concentration polarizations. All of these will contribute to the decrease of the *external voltage V* of the Fuel Cells and to the increase of the "speed" of the process, actually measured by the density of the electrical current *i*.

Ohmic polarization is simple to be understood, because it represents the decrease of voltage caused by the conversion of electrical energy into heat (Joule effect), when electricity is passing through an electrical internal cell resistance (of the electrolyte) R_i. We present here the simplified case in which the two irreversibilities generated by the two other polarizations, Activation and Concentration ones, are neglected. In the next paragraph all the three ireversibilities will be taken into consideration.

When the circuit is closed and an electrical current I is passing through an external resistance R_e (of the bulb - fig. 3), the actual output voltage V is:

$$V = V^o - IR_i \tag{26}$$

The electrical power P_e obtained from the Fuel Cell which is used for lighting a bulb (fig. 3) having the external resistance R_e, where finally the chemical energy of the fuel H_2 is converted into light and heat, is:

$$\dot{W}_e = V \cdot I = R_e \cdot I^2 \tag{27}$$

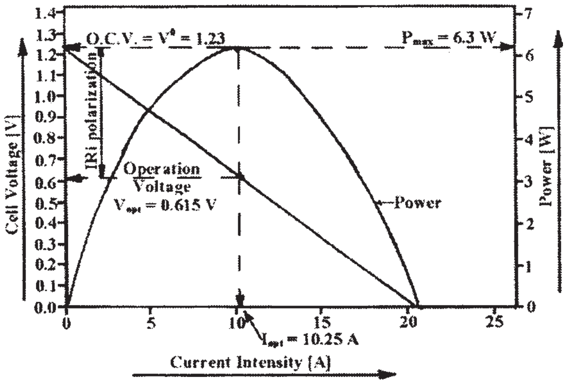

Fig. 4. Voltage – Current Intensity and Power curves for Hydrogen – Oxygen Fuel Cell [65]

where Ohm's Law is used:

$$V = R_e I \tag{28}$$

In figure 4 the external Voltage *V* is decreasing with the increase of external electrical current I, because of Ohmic polarization $I \cdot R_i$. By consequence, the electrical Power W_e first increases, attains a maximum W_{max} = 6.3 W and after that decreases to zero. When the Power reaches maximum, this corresponds to an Optimum Intensity of the Current I_{opt}.

Similarities between the irreversibilities in Electrochemical Systems (Battery or Fuel Cell) and irreversibilities in a Thermo-Mechanical Systems (a gas in a cylinder-piston Thermal Machine)

The reversible work of an Electrochemical Fuel Cell is:

$$\dot{W}_{rev} = -\Delta G = (OCV) \cdot n \cdot F \tag{29}$$

The Reversible Open Circuit Voltage (OCV) is:

$$(OCV)_{rev} = \frac{-\Delta G}{n \cdot F} = V^{o} \tag{30}$$

The Irreversible Voltage $V_{D,ir}$ in a discharge process (conversion of Gibbs Potential into electrical work) is [48-55]:

$$V_{D,ir} = (OCV)_{rev} - I \cdot \sum R_{int,cell} - \eta_{ca} - \eta_{cc} - \eta_{aa} - \eta_{ac} \tag{31}$$

The Irreversible work $\dot{W}_{ir}$ in a discharge process will be:

$$\dot{W}_{ir} = V_{D,ir} \cdot n \cdot F = (OCV)_{rev} \cdot n \cdot F \cdot \left[1 - \frac{I \cdot \sum R_{int,cell}}{(OCV)_{rev}} - \frac{\sum \eta_i}{(OCV)_{rev}}\right] \tag{32}$$

For activation polarization, η_a with values less than *RT*/*nF*, a simplified expression can be used [43, 48-55]:

$$\eta_a = \frac{RT}{nF} \cdot \frac{i}{i_o} \tag{33}$$

where: i_o = density of exchange current at electrodes, and i = density of the (external) current.

The concentration polarization can be expressed also as function of the ratio between "two speeds", namely: the density of the current i and the limiting current i_L, as follows [43, 48-55]:

$$\eta_c = \frac{RT}{nF} \cdot \ln \frac{i_L}{i_L - i} = \frac{RT}{nF} \cdot \ln \frac{1}{1 - \frac{i}{i_L}} \cong \frac{RT}{nF} \ln\left(1 + \frac{i}{i_L}\right) \tag{34}$$

For the cases when $i < i_L$, a simplified expression can be obtained [43, 48-55]:

$$\eta_c \cong \frac{RT}{nF} \cdot \frac{i}{i_L} \tag{35}$$

With (33) and (35) in (32), W_{irr} becomes [29, 26, 55, 45]:

$$W_{irr} = \left[1 \pm \frac{I \cdot \sum R_{int}}{(OCV)_{rev}} \pm \frac{RT}{(OCV)_{rev} \cdot n \cdot F}\left(\frac{i}{i_{L,a}} + \frac{i}{i_{L,c}}\right) \pm \pm \frac{RT}{(OCV)_{rev} \cdot n \cdot F}\left(\frac{i}{i_{O,a}} + \frac{i}{i_{O,c}}\right)\right] \cdot W_{rev} \tag{36}$$

with the signs: (-) for the discharging process and (+) for the charging process.

The equation (36) is similar to that corresponding to the expression of the irreversible work in a process of compression or expansion of a gas in a cylinder, with Finite Speed of the piston, with Throttling (friction of the gas passing through a porous medium) and with Friction between piston and cylinder [24, 25, 27, 29]:

$$\delta W_{irr} = P_{m,i} \cdot \left(1 \pm \frac{aw}{c} \pm b \cdot \frac{\Delta P_{th}}{2 P_{m,i}} \pm \frac{\Delta P_f}{P_{m,i}}\right) dV \tag{37}$$

But $\delta W_{rev} = P \cdot dV$, so:

$$\delta W_{rev} = \left(1 \pm \frac{\Delta P_f}{P_m} \pm \frac{b \cdot \Delta P_{thr}}{2 \cdot P_m} \pm \frac{a \cdot w}{c}\right) \cdot \delta W_{rev} \tag{38}$$

with the sign: (-) for expansion or (+) for compression

The same mathematical format of eq. (38) and eq. (36) is quite obvious. Based on this "formal mathematical similarity" we can expect that there is also a physical analogy between the two classes of phenomenon.

First of all, the signs in parenthesis are changed function on the fact that the energy is introduced in the system (compression in TM or charging in ED) or energy is extracted from the system (expansion in TM or discharging in ED).

Secondly, every term inside of eq. (36) and (38) has a correspondent:

- the term $\frac{I \cdot \sum R_{int}}{(OCV)_{rev}}$ which reflects the irreversibility generated by the "friction" of the electrons in the time of their motion through internal resistors ΣR_{int}, has a correspondent in the term $\frac{\Delta P_f}{P_m}$ which takes into account the friction between the piston and the cylinder;
- the term $\frac{RT}{(OCV)_{rev} \cdot n \cdot F}\left(\frac{i}{i_{La}} + \frac{i}{i_{L,c}}\right)$ which reflects the irreversibility generated by the ions' diffusion process, which moves towards the electrons in the electric field, i has a correspondent in the term $\frac{b \cdot \Delta P_{thr}}{2 \cdot P_m}$ which takes into account the irreversibility generated by the movement of the

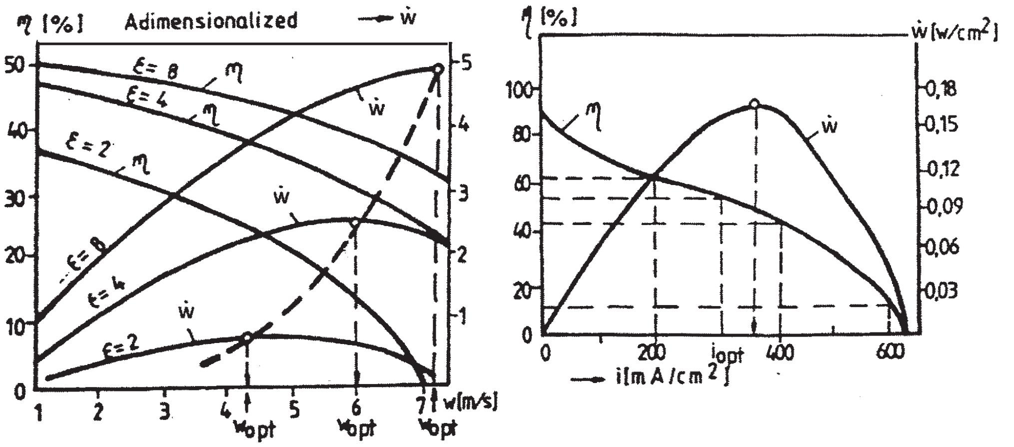

Fig. 5. Comparison between the Efficiency and Power curves for a Stirling Engine (a) and a Fuel Cell (b) [29]

molecules through internal tubes or porous material of a regenerator (throttling process), which implies a pressure loss ΔP_{thr};

- the term $\frac{RT}{(OCV)_{rev}\cdot n\cdot F}\left(\frac{i}{i_{0,a}}+\frac{i}{i_{0,c}}\right)$ which reflects the irreversibility generated by the electrode reactions with finite speed of the electrons (the density of current i - finite), has a correspondent in the term $\frac{a\cdot w}{c}$, which takes into account the irreversibility generated by the finite speed of the piston *w* (and also of the process).

The importance of this approach and the discovery of the analogy we have just mentioned above, consists in the fact that *Electrochemical Devices* and *Thermal Machines* can be treated on the same fundamental basis and concepts, related to the First Law of Thermodynamics (combined with the Second Law) developed for processes with Finite Speed (*i* for ED or *w* for TM), or developed for processes in finite time.

The expressions of *Efficiency* and *Power*

We have studied several cycles with finite speed and have shown that in all these cases (Carnot, Otto, Stirling cycles) the efficiency and the power have a similar format:

$$\eta_{th} = \eta_{rev}\cdot\eta_{II,ir(a)}\cdot\eta_{II,ir(b)}\cdot\eta_{II,ir(c)} \qquad (39)$$

where:

η_{th} – thermal Efficiency of a cycle;

η_{rev}– Efficiency of the reversible cycle;

$\eta_{II,\,ir(a,b,c)}$ - irreversible Efficiency due to different causes (or mechanisms) of irreversibilities (a, b, c).

This format has been suggested by Bejan [32] for Thermal Machines, and it is very interesting to notice that this format is also valid for Fuel Cells [26, 27, 29, 47].

$$\eta_{el} = \eta_{rev}\cdot\eta_{II,ir} = \eta_{izot}\cdot\eta_{II,ir} \qquad (40)$$

where:

η_{el}= Electrical Efficiency of the Fuel Cell or Battery;

$\eta_{rev} = \eta_{izot}$ Reversible Efficiency = Isothermal Isobaric Efficiency;

$\eta_{II,\,ir}$ = irreversible efficiency generated by the electrochemical processes with finite density current i.

$$\eta_{II,ir,FC} = 1-\sum\frac{\eta_{pol}}{E_{rev}} \qquad (41)$$

$$\eta_{II,ir,Bat} = \frac{1-\sum\frac{\eta_{pol}}{E_{rev}}}{1+\sum\frac{\eta_{pol}}{E_{rev}}} \qquad (42)$$

The Power of a thermal engine cycle will be:

$$\dot{W} = Q_{hs}\cdot\eta_{th}\cdot\frac{n_r}{60} \qquad (43)$$

where:

Q_{hs} - heat at the source of the engine;

n_r - rotation speed.

The trend of the curve η_{th} = F(w) is always like in figure 5 and the maximum of η_{th} corresponds to zero speed; but the trend of W = F(w) always has a maximum, which corresponds to the optimum value of the speed w_{opt} or efficiency $\eta_{r,opt}$.

The Power of a Fuel Cell or a Battery:

$$\dot{W}_{FC,Bat} = \eta_{el}\cdot E_{rev}\cdot I \qquad (44)$$

will also have a maximum for an optimum current I or optimum density of the current *i*.

The electrical efficiency of a Fuel Cell or a Battery has a completely similar aspect like the efficiency of a thermal cycle (or thermal cycle engine). Using this method of optimization, we could express the Efficiency and Power of a cycle not only as a function of the speed but also as a function of some important dimensions of the engine. For example, for a Stirling Solar Engine Petrescu et al. [39] have done this with respect to the diameter of the tubes of Solar Receiver of Concentrated Radiation and simultaneously optimized the speed of the engine and also its diameter *d* for different thermal engines (using as a working fluid air, helium or hydrogen).

In conclusion, the analogy pointed out in this section permits a unified approach for optimization of thermal machines and electrochemical devices starting with the new expressions for the First Law for processes with Finite Speed. This Direct Method could be the starting point of a new Non–Linear Irreversible Thermodynamics because, as we have shown in this section, two different fields have been studied with the same method.

Conclusions

The importance and significance of the Direct Method from Finite Speed Thermodynamics (FST) applied to Thermal Machines and also Electrochemical Devices.

The method of analysis called by us the Direct Method proceeds from a basis of Thermodynamics Fundamentals, detailed and developed systematically, starting from an unique equation (4) or (14), with The Equation of The First Law of Thermodynamics for Finite Speed Processes, combined with the Second Law. In order to shorten this expression, in all of our papers and books, we have used the expression: The First Law of Thermodynamics for Finite Speed Processes.

The most important advantages of the method developed in the framework of TFS, in comparison to TFT, is that it is capable of being Validated and it explains and contains quantitatively both the causes and mechanisms of irreversibility generation in complex cycles or real machines such as Stirling Machines (Refrigerators, Heat Pumps, Solar Stirling Engines), as well as in other cycles like: Otto, Diesel, Brayton and Carnot. The explanation of this success consists in the fact that TFS takes into account both kinds of causes of irreversibilities: internal and external, all of them expressed as a function of the speed and other parameters, in the same unique Fundamental Equations: eq. (4) - for Simple Systems or for complex Systems [9, [10, 23, 24]. This unified approach is extremely important in the case of complex installations where both Thermal Machines (TM) are combined with Electrochemical Devices (ED). Such *Complex Systems* are for example the SEHE-Systems (as Petrescu et al. [55] introduced them). In a recent paper, that the authors have used and developed recently [38], this approach for Optimization of Solar Stirling Engines, producing electricity - used in an Electrolyser, producing Hydrogen - stored by compression and used by night in Fuel Cells, for producing backup electricity. A similar approach can be done in Optimization of Hybrid Cars where a Thermal Machine (internal combustion engine) is combined with an Electrochemical Device (a Fuel cell or a High Capacity Battery), increasing the total efficiency and also decreasing pollution.

Nomenclature

c - average molecular speed, m/s
CC - combustion chamber
C_p - specific heat at constant pressure
C_v - specific heat at constant volume
E_r - electromotive balance force, V
F - Faraday constant
FC - fuel cell
ΔG - Gibbs potential, J
HE - heat engine
ΔH - enthalpy of reaction, J
I - electrical current, A
i - current density i= I/A
k - adiabatic exponent
K_1 - constant (depends on properties of the gas)
n - gram-moles of electrons
P - pressure, Pa
Q - heat, J
R_e - external electrical resistance, Ω
ΔS - entropy of reaction, J K^{-1}
T - temperature, K
U - internal energy, J
V - Volume, m^3
A - Area, m^2
w - speed, m/s
W - work, J
W - power, W

Greek symbols

η - efficiency

Subscripts

I - First Law
II - Second Law
0 - standard parameters
Bat - Battery
C - reversible Carnot Cycle
el - electrical
H - hot-end of the machine
i - instantaneous
ir - irreversible
L - low temperature end of the machine
m -average
med -average
max - maximum
rev - reversible
p - piston
thr - throttling

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