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Modelling and optimization of static and dynamic power systems

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Abstract

This research treats power optimization for energy converters, such like thermal, solar and chemical engines. Thermodynamic analyses lead to converter's efficiency and limiting power. Steady and dynamic systems are investigated. Static optimization of steady systems applies the differential calculus or Lagrange multipliers, dynamic optimization of unsteady systems uses variational calculus and dynamic programming. The primary result of the first is the limiting value of power, whereas that of the second is a total generalized work potential. The generalizing quantity depends on thermal coordinates and a dissipation index, h, i.e. the Hamiltonian of the problem of minimum entropy production. It implies stronger bounds on work delivered or supplied than the classical work of thermodynamics.

1 Introduction

In this research we treat power limits in static and dynamical energy systems driven by fluids that are generally restricted in their amount or magnitude of flow, i.e. are certain resources. A power limit is an upper (lower) bound on power produced (consumed) in the system. A resource is a valuable substance or energy used in a process; its value can be quantified by specifying its exergy, a maximum work obtained when the resource relaxes to the equilibrium. Reversible relaxation of the resource is associated with the classical exergy. When dissipative phenomena prevail generalized exergies arise which quantify deviations of the system's efficiency from the Carnot efficiency. An exergy is obtained as the principal component of solution to the variational problem of extremum work under suitable boundary conditions. Other components of the solution are the optimal trajectory and optimal control. In thermal systems without chemical changes the trajectory is characterized by the temperature of the resource fluid, $T(t)$, whereas the control, is an innovative quantity, called Carnot temperature $T'(t)$. This control was defined in our previous work [1,2] to get rid less suitable while more popular controls such as heat flux or temperatures of circulating fluids (Fig.1) which are constrained by balances of mass and entropy. In opposition to these conventional controls Carnot temperature is a free control. For the engine in Fig. 1 Carnot temperature is

$$T' \equiv T_2 T_{1'} (T_{2'})^{-1} .$$

In chemical case also Carnot chemical potential(s) μ'(t) enter

$$\frac{\mu'}{T'} = \frac{\mu_2}{T_2} + \frac{T_{2'}}{T_2}\left(\frac{\mu_{1'}}{T_{1'}} - \frac{\mu_{2'}}{T_{2'}}\right) .$$

Whenever $T'(t)$ and $\mu'(t)$ differ from $T(t)$ and $\mu(t)$ then the power-producing resource relaxes with a finite rate, and with an efficiency vector different from the perfect efficiency. Only when $T' = T$ and $\mu' \doteq \mu$ the efficiency is pefect, but this corresponds with an infinitely slow relaxation rate of the resource to the thermodynamic equilibrium. Carnot variables T' and μ' are two free, independent control variables applied in power maximization of steady and dynamical generators.

The structure of this paper is as follows. Section 2 discusses various aspects of optimization with resources. Properties of steady systems are outlined in Sec. 3, whereas those of dynamical ones - in Sec. 4. Section 5 develops analyses of power yield with resource downgrading (in the first reservoir) and outlines origin of "work potentials" for finite rates. Sections 6-8 discuss various Hamilton-Jacobi-Bellman equations (HJB equations) for optimal work functions, as solutions of power yield problems. Extensions for fuel cells as electrochemical flow systems are outlined in Sec. 9.

The size limitation of the paper does not allow for inclusion of all derivations to make the paper self-contained, thus the reader may need to turn to some previous works, [1] - [5] of which ref. [3] discusses convergence of numerical algorithms solving HJB equations and role of Lagrange multipliers.

2 Thermodynamic Aspects of Finite Resources

Limited amount or flow of a resource working in an engine causes a decrease of the resource potential in time (chronological or spatial). This is why studies of the resource downgrading apply the dynamical optimization methods. From the optimization viewpoint, dynamical process is every one with sequence of states, developing either in the chronological time or in (spatial) holdup time. The first group refers to unsteady processes in non-stationary systems, the second group may involve steady state systems.

In a process of energy production two resting reservoirs do interact through an energy generator (engine). In this process power flow is steady only when two reservoirs are infinite. When one, say, upper, reservoir is finite, its potential must decrease in time, a result from the energy balance. Any finite reservoir is thus a resource reservoir. It is the resource property that leads to the dynamical behavior of the fluid and its relaxation to the equilibrium with an infinite lower reservoir (usually the environment).

Alternatively, fluid at a steady flow can replace resting upper reservoir. The resource downgrading is then a steady-state process in which the resource fluid flows through a pipeline or stages of a cascade and the fluid's state changes along a steady trajectory. As in the previous case the trajectory is a curve describing the fluid's relaxation towards the equilibrium between the fluid and the lower reservoir (the environment). This is sometimes called "active relaxation" as it is associated with the simultaneous work production. It should be contrasted with "dissipative relaxation", a well-known, natural process between a body or a fluid and the environment without any power production. Relaxation (either active or dissipative) leads to a decrease of the resource potential (i.e. temperature) in time. An inverse of the relaxation process is the one in which a body or a fluid abandons the equilibrium. This cannot be spontaneous; rather the inverse process needs a supply of external power. This process refers to thermal upgrading of the resource, which can be accomplished with a heat pump.

3 Power and Power Limits in Steady Systems

The great deal of research on power limits published to date deals with stationary systems, in which case both reservoirs are infinite. To this case refer steady-state analyses of the Chambadal-Novikov-Curzon-Ahlborn engine (CNCA engine [6]), in which energy exchange is described by Newtonian law of cooling, or the Stefan-Boltzmann engine, a system with the radiation fluids and the energy exchange governed by the Stefan-Boltzmann law [7].

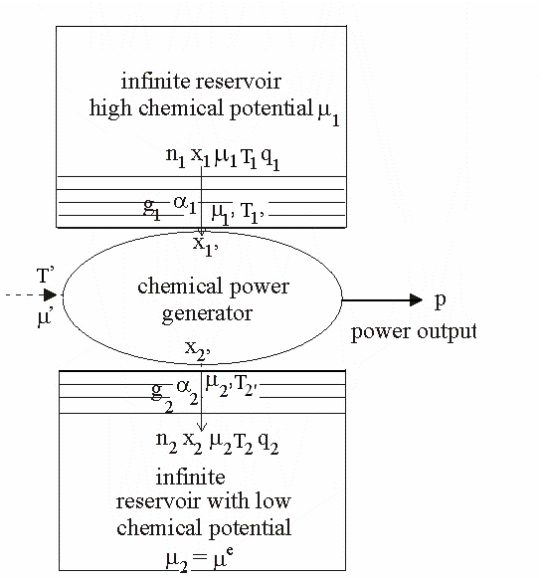

Fig. 1. A scheme of an engine controlled by a suitable choice of Carnot variables $T'$and μ'.

Due to their stationarity (caused by the infiniteness of both reservoirs), controls maximizing power are lumped to a fixed point in the state space. In fact, for the CNCA engine, the maximum power point may be related to the optimum value of a free (unconstrained) control variable which can be efficiency η or Carnot temperature T'. In terms of the reservoirs temperatures T_1 and T_2 and the internal irreversibility factor Φ one finds $T'_{opt} = (T_1 \Phi T_2)^{1/2}$ [4]. For the Stefan-Boltzmann engine exact expression for the optimal point cannot be determined analytically, yet, this temperature can be found graphically from the chart $P=f(T')$. Moreover, the method of Lagrange multipliers can successfully be applied [8]. As their elimination from a set of resulting equations is quite easy, the problem is broken down to the numerical solving of a nonlinear equation for the optimal control T'. Finally, the so-called pseudo-Newtonian model [4, 5], which uses state or temperature dependent heat exchange coefficient, $\alpha(T^3)$, omits, to a considerable extent, analytical difficulties associated with the Stefan-Boltzmann equation. Applying this model in the so-called symmetric case, where both reservoirs are filled up with radiation, one shows that the optimal (power maximizing) Carnot temperature of the steady radiation engine is that for the CNCA engine, i.e. [4]. This equation is, in fact, a good approximation under the assumption of transfer coefficients dependent solely on bulk temperatures of reservoirs.

4 Power and Its Limits in Dynamical Systems

Dynamical energy yield requires the knowledge of an extremal curve rather than an extremum point, i.e. is associated with application of variational metods in place of static optimization methods. For example, the use of the pseudo-Newtonian model to quantify the dynamical energy yield from radiation, gives rise to an extremal curve describing the radiation relaxation to the equilibrium. This curve is non-expotential, the consequence of the nonlinear properties of the relaxation dynamics. Non-expotential are also other curves describing the radiation relaxation, e.g. those following from exact models using the Stefan-Boltzmann equation (symmetric and hybrid, [4,5]).

Analytical difficulties associated with dynamical optimization of nonlinear systems are severe; this is why diverse models of power yield and diverse numerical approaches are applied. Optimal (e.g. power-maximizing) relaxation curve $T(t)$ is associated with the optimal control curve $T'(t)$; they both are components of the dynamic optimization solution to a continuous problem. In the corresponding discrete problem, formulated for numerical purposes, one searches for optimal temperature sequences $\{T^n\}$ and

$\{T'^{n}\}$. Various discrete optimization methods involve: direct search, dynamic programming, discrete maximum principle, and combinations of these methods.

Minimum power supplied to the system is described by function sequences $R^n(T^n, t^n)$, whereas maximum power produced – by functions $V^n(T^n, t^n)$. Importantly, energy limits of dynamical processes are connected with the exergy functions, the classical exergy and its rate-dependent extensions. To obtain classical exergy from power functions it suffices to assume that the thermal efficiency of the system is identical with the Carnot efficiency. Yet, non-Carnot efficiencies lead to generalized exergies. The latter depend not only on the classical thermodynamic variables but also on their rates. These generalized exergies refer to state changes in a finite time, and can be contrasted with the classical exergies that refer to reversible quasistatic processes evolving infinitely slowly. The benefit obtained from generalized exergies is that they define stronger energy limits than those predicted by classical exergies. In this case Fig. 1 above is suitably applied to calculation of dynamical systems. Introduced is a cascade of engines, where each stage is controlled by suitable choice of Carnot variables T' and μ'. The system stage comprises: a resource at flow, engines and the environment. At each stage power is generated and total flux of resulting power is maximized. In the chemical case the control is the propelling mass flux of the fuel flowing to the power generator.

5 Finite-Rate Exergies as Work Potentials

Two different works, the first associated with the resource downgrading during its relaxation to the equilibrium and the second – with the reverse process of resource upgrading, are essential. During the approach to the equilibrium engine mode takes place in which work is released, during the departure-heat-pump mode occurs in which work is supplied. Work W delivered in the engine mode is positive by assumption ("engine convention"). Sequence of irreversible engines such as the one in Fig.1 (CNCA or Stefan-Boltzmann engines) serves to determine a rate-dependent exergy extending the classical exergy for irreversible, finite rate processes. Before maximization of a work integral, process efficiency η has to be expressed as a function of state T and a control, i.e. energy flux q or rate $\mathrm{d}T/\mathrm{d}\tau$, to assure the functional property (path dependence) of the work integral. The integration must be preceded by maximization of power or work at flow (the ratio of power and flux of driving substance) w to assure an optimal path. The optimal work is sought in the form of a potential which depends on the end states and duration. For appropriate boundary conditions, the principal function of extremum work coincides with the notion of an exergy, the function that characterizes quality of resources.

The idea of an infinite number of infinitesimal CNCA steps, necessary for exergy calculations, can be developed. Each step is a work-producing (consuming) stage with the energy exchange between two fluids and the thermal machine through finite "conductances". For the radiation engine it follows from the Stefan-Boltzmann law that the effective transfer coefficient α_1 of the radiation fluid is necessarily temperature dependent, $\alpha_1 = \propto T_1^3$. The second or low-T fluid represents the usual environment, as defined in the exergy theory. This fluid possesses its own boundary layer as a dissipative component, and the corresponding exchange coefficient is α_2. In the physical space, the flow direction of the resource fluid is along the horizontal coordinate l. The optimizer's task is to find an optimal temperature of the resource fluid along the path that extremizes the work consumed or delivered.

Total power obtained from an infinite number of small engines is determined as the Lagrange functional

$$\dot{W}[\mathbf{T}^i, \mathbf{T}^f] = \int_{t^i}^{t^f} f_0(T, T')dt = -\int_{t^i}^{t^f} \dot{G}c(T)\eta(T, T')\dot{T}dt \tag{1}$$

where f_0 is power generation intensity, $\dot{G}$ - resource flux, $c(T)$-specific heat, $\eta(T, T')$ -efficiency in terms of state T and control T, further $\mathbf{T}$ − enlarged state vector comprising state and time, t −time variable (residence time or holdup time) for the resource contacting with heat transfer surface. Sometimes one uses a non-dimensional time τ, identical with the so-called number of the heat transfer units. Note that,

for constant mass flow of a resource, one can extremize power per unit mass flux, i.e. the quantity of work dimension called "work at flow". In this case Eq. (1) describes a problem of extremum work. When the resource flux is constant a work functional describing the thermal exergy flux per unit flux of resource can be obtained from Eq. (1)

$$w_{\max\limits_{dT/dt}} = -\int_{T^i=T}^{T^f=T^e} c(T)\left(1-\frac{T^e}{T'(T,dt/dT)}\right)dT\ . \tag{2}$$

Note that the independent variable in this equation is T, i.e. it is different than that in Eq. (1). The function f_0 in Eq. (1) contains thermal efficiency function, η, described by a practical counterpart of the Carnot formula. When $T > T^e$, efficiency η decreases in the engine mode above η_C and increases in the heat-pump mode below η_C. At the limit of vanishing rates, $dT/dt = 0$ and $T' \to T$. Then work of each mode simplifies to the common integral of the classical exergy. For the classical thermal exergy

$$w_{\max\limits_{dT/dt\to 0}} = -\int_{T^i=T}^{T^f=T^e} c(T)\left(1-\frac{T^e}{T}\right)dT = h-h^e-T^e(s-s^e)\,. \tag{3}$$

Nonlinearities can have both thermodynamic and kinetic origins; the former refer, for example, to state dependent heat capacity, $c(T)$, the latter to nonlinear energy exchange. Problems with linear kinetics (Newtonian heat transfer) are an important subclass. In problems with linear kinetics, fluid's specific work at flow, w, is described by an equation

$$w[\mathbf{T}^i,\mathbf{T}^f] = \dot{W}/\dot{G} = -\int_{T^i}^{T^f} c(T)\left(1-\frac{T^e}{T}\right)dT - T^e\int_{t^i}^{t^f} c(T)\frac{(T'-T)^2}{T'T}\,d\tau \tag{4}$$

where

$$\tau \equiv \frac{x}{H_{TU}} = \frac{\alpha' a_v F}{\dot{G}c}\,x = \frac{\alpha' a_v F v}{\dot{G}c}\,t = \frac{t}{\chi} \tag{5}$$

is non-dimensional time of the process. Equation (5) assumes that a resource fluid flows with velocity v through cross-section F and contacts with the heat transfer exchange surface per unit volume a_v [1]. Quantity τ is identical with the so-called number of the heat transfer units.

Solutions to work extremum problems can be obtained by:
a) variational methods, i.e. via Euler-Lagrange equation

$$\frac{\partial L}{\partial T} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{T}}\right) = 0\ . \tag{6}$$

In the example considered above, i.e. for a linear thermal system

$$T\frac{d^2T}{d\tau^2} - \left(\frac{dT}{d\tau}\right)^2 = 0 \tag{7}$$

which corresponds with the optimal trajectory

$$T(\tau,\tau^f,T^i,T^f) = T^i(T^f/T^i)^{\tau/\tau^f}\ . \tag{8}$$

($\tau^i = 0$ is assumed in Eq. (8).) However, the solution of the Euler-Lagrange equation does not provide any information about the optimal function V. Hence another method must be used as described below.
b) dynamic programming via Hamilton-Jacobi-Bellman equation (HJB equation, [9]) for the 'principal function' (V or R), also called extremum work function. This is described below.

6 HJB Equations for Selected Power Systems

For the linear kinetics considered

$$\frac{\partial V}{\partial \tau} - \max_{T'}\left\{(-\frac{\partial V}{\partial T} - c(1-\frac{T^e}{T'}))(T'-T)\right\} = 0\,. \tag{9}$$

The extremal work function V is a function of the final state and total duration. After evaluation of optimal control and its substitution to Eq. (9) one obtains a nonlinear equation

$$\frac{\partial V}{\partial \tau} - c\left\{\sqrt{T^e} - \sqrt{T(1+c^{-1}\partial V/\partial T)}\right\}^2 = 0 . \tag{10}$$

which is the Hamilton-Jacobi equation of the problem. Its solution can be found by the integration of work intensity along an optimal path, between limits T^i and T^f. A reversible, path independent part of V is the classical exergy $A(T, T^e, 0)$. Details of models of multistage power production in sequences of engines are known from previous papers [1]-[5].

We shall display further some Hamilton-Jacobi-Bellman equations for power systems described by nonlinear kinetics. A suitable example is a radiation engine whose power integral is approximated by a pseudo-Newtonian model of radiative energy exchange associated with optimal function

$$V(T^i,t^i,T^f,t^f) \equiv \max_{T'(t)}\left(-\int_{t^i}^{t^f} \dot{G}_m c_m (1-\Phi'\frac{T^e}{T'}) \upsilon\,(T',T)dt \right) \tag{11}$$

where $\upsilon = \alpha(T^3)(T'-T)$. An alternative form uses Carnot temperature T' explicit in υ [5]. Optimal power (11) becomes

$$\dot{W} = -\int_{T}^{T_0} \dot{G}_m \left(c_{hm}(T) - c_{vm}(T)\frac{T^e}{T} \right) \upsilon dt - \int_{T}^{T_0} T^e \dot{G}_m \left(c_{vm}(T)\left(\frac{\chi\upsilon^2}{T(T+\chi\upsilon)} + (1-\Phi)\frac{\upsilon}{T+\chi\upsilon}\right)\right) dt . \tag{12}$$

This process is described by a pseudolinear kinetics $dT/dt = f(T, T')$ consistent with $\upsilon = \alpha(T^3)(T'-T)$ and a general form of HJB equation for work function V in the form

$$. \quad -\frac{\partial V}{\partial t} + \max_{T'(t)}\left(f_0(T,T') - \frac{\partial V}{\partial T} f(T,T') \right) = 0 \tag{13}$$

where f_0 is defined as the integrand of Eq. (11) or (12).

A more exact model or radiation conversion relaxes the assumption of the pseudo-Newtonian transfer and applies the Stefan-Boltzmann law. For a *symmetric* model of radiation conversion (both reservoirs composed of radiation)

$$\dot{W} = \int_{t^i}^{t^f} \dot{G}_c(T)\left(1-\frac{\Phi T^e}{T'}\right)\beta\frac{T^a - T'^a}{(\Phi'(T'/T^e)^{a-1}+1)T^{a-1}}dt . \tag{14}$$

The coefficient is $\beta = \sigma a_v c_h^{-1}(p_m^0)^{-1}$ is related to molar constant of photons density p_m^0 and Stefan-Boltzmann constant σ. In the physical space, power exponent a=4 for radiation and a=1 for a linear resource. With a state equation

$$\frac{dT}{dt} = -\beta\frac{T^a - T'^a}{(\Phi'(T'/T_2)^{a-1}+1)T^{a-1}} \tag{15}$$

[5] applied in general Eq. (13) we obtain a *HJB* equation

$$-\frac{\partial V}{\partial t} + \max_{T'(t)}\left\{\left(\dot{G}_c(T)(1-\Phi\frac{T^e}{T'}) + \frac{\partial V}{\partial T}\right)\beta\frac{T^a - T'^a}{(\Phi'(T'/T_2)^{a-1}+1)T^{a-1}}\right\} = 0 . \tag{16}$$

Dynamics (15) is the characteristic equation for Eq. (16).

For *a hybrid model* of radiation conversion (upper reservoir composed of the radiation and lower reservoir of a Newtonian fluid, [5]) the power is (17)

$$\dot{W} = -\int_{\tau'}^{t^f} G_c(T)\left(1 - \frac{\Phi T^e}{(T^a + \beta^{-1}T^{a-1}u)^{1/a} + \Phi\beta^{-1}T^{a-1}ug_1/g_2}\right)u dt \tag{17}$$

and the corresponding Hamilton-Jacobi-Bellman equation is

$$-\frac{\partial V}{\partial t^f} + \max_{T'(t)}\left\{-\left(\dot{G}_c(T)(1 - \frac{\Phi T^e}{(T^a + \beta^{-1}T^{a-1}u)^{1/a} + \Phi\beta^{-1}T^{a-1}ug_1/g_2}) + \frac{\partial V}{\partial T^f}\right)u\right\} = 0\,. \tag{18}$$

7 Some Analytical Solutions of HJB Equations

In all HJB equations extremized expressions are some Hamiltonians, H. The maximization of H leads to two equations. The first expresses optimal control T' in terms of T and $z = -\partial V/\partial T$. For the linear kinetics of Eq. (9) we obtain

$$\frac{\partial V}{\partial T} - \frac{\partial f_0(T,T')}{\partial T'} = \frac{\partial V}{\partial T} + c(1 - \frac{T^e T}{T'^2}) = 0 \tag{19}$$

whereas the second is the original equation (9) without maximizing operation

$$\frac{\partial V}{\partial t} + \frac{\partial V}{\partial T}(T' - T) + c(1 - \frac{T_2}{T'})(T' - T) = 0\,. \tag{20}$$

To obtain optimal control function $T'(z, T)$ one should solve the second equality in equation (19) in terms of T', The result is Carnot control T' in terms of T and $z = -\partial V/\partial T$,

$$T' = \left(\frac{T^e T}{1 + c^{-1}\partial V/\partial T}\right)^{1/2}\,. \tag{21}$$

This is next substituted into (20); the result is the nonlinear Hamilton-Jacobi equation

$$-\frac{\partial V}{\partial \tau} + cT\left(\sqrt{1 + c^{-1}\partial V/\partial T} - \sqrt{T^e/T}\right)^2 = 0 \tag{22}$$

which contains the energylike (extremum) Hamiltonian

$$H(T, \frac{\partial V}{\partial T}) = cT\left(\sqrt{1 + c^{-1}\partial V/\partial T} - \sqrt{T^e/T}\right)^2\,. \tag{23}$$

Expressing extremum Hamiltonian (23) in terms of state variable T and Carnot control T' yields an energylike function satisfying the following relations

$$E(T,u) = f_0 - u\frac{\partial f_0}{\partial u} = cT^e\frac{(T' - T)^2}{T'^2} \tag{24}$$

E is the Legendre transform of the work lagrangian $l_0 = -f_0$ with respect to the rate $u = \mathrm{d}T/\mathrm{d}\tau$.

Assuming a numerical value of the Hamiltonian, say h, one can exploit the constancy of H to eliminate $\partial V/\partial T$. Next combining equation $H=h$ with optimal control (21), or with an equivalent result for energy flow control $u=T'-T$

$$u = \left(\frac{T^e T}{1 + c^{-1}\partial V/\partial T}\right)^{1/2} - T\,. \tag{25}$$

yields optimal rate $u = \dot{T}$ in terms of temperature T and the Hamiltonian constant h. An optimal trajectory which applies to systems with internal dissipation (factor Φ) and applies to the pseudo-Newtonian model of radiation has the form

$$\dot{T} = \left(\pm \sqrt{\frac{h_\sigma}{\Phi c_v(T)}} \left(1 - \pm \sqrt{\frac{h_\sigma}{\Phi c_v(T)}} \right)^{-1} \right) T \equiv \xi(h_\sigma, \Phi, T) T \quad , \tag{26}$$

where ξdefined in the above equation, is an intensity index and $h_\sigma = h/T$. This holds for the temperature dependent heat capacity $c_v(T)=4a_0T^3$. Positive ξ refer to heating of the resource fluid in the heat-pump mode, and the negative - to cooling of this fluid in the engine mode. Thus, the optimal power is associated with the temperature relaxation

$$\dot{T} = \xi(h_\sigma, T, \Phi) T \tag{27}$$

Equations (26 and (27) describe the optimal trajectory in terms of variables T and h. The related optimal (Carnot) control is

$$T' = \left(1 + \xi(h_\sigma, \Phi, T)\right) T \tag{28}$$

Thus, in comparison with the linear systems, the pseudo-Newtonian relaxation is not exponential.

9 Some Data for Electrochemical Systems

In chemical engines mass transports participate in transformation of chemical affinities into mechanical power [10-13]. Yet, in chemical and electrochemical engines generalized reservoirs are present, capable of providing both heat and substance. Fuel cells are electrochemical engines propelled by chemical reactions. Units producing power are engines, whereas those which consume power are electrolyzers. Their main advantage in comparison to heat engines is that their efficiency is not a major function of device size. Figure 2 illustrates a solid oxide fuel cell (SOFC) which works in the power yield mode.

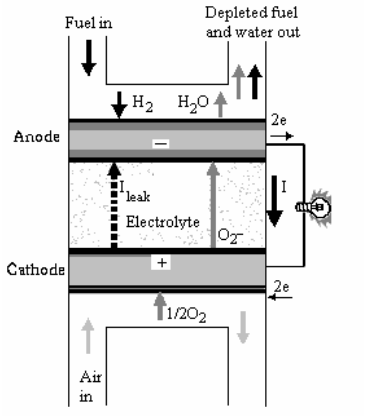

Fig. 2. Principle of a solid oxide fuel cell

The basic structure of fuel cells includes electrolyte layer in contact with a porous anode and cathode on either side. Gaseous fuels are fed continuously to the anode (negative electrode) compartment and an oxidant (i.e., oxygen from air) is fed to the cathode (positive electrode) compartment. Electrochemical reactions at the electrodes produce an electric current. The effect is the oxidation of fuel, e.g. hydrogen, and reduction of oxidant, e.g. oxygen. This makes fuel cells similar to an engine in Fig. 1.

Voltage lowering in fuel cells below the idle run value is a suitable measure of their imperfection, Fig.3. With the concept of effective resistances operating voltage of a fuel cell can be represented as the departure from the idle run voltage E_0 [14]

$$V = E_0 - V_{\text{int}} = E - V_{\text{act}} - V_{\text{conc}} - V_{\text{ohm}} \tag{29}$$

The losses, called polarization, include three main sources: activation polarization (V_{act}), ohmic polarization (V_{ohm}), and concentration polarization (V_{conc}). Large number of approaches for calculating polarization losses has been reviewed [15]. Activation and concentration polarization occurs at both electrodes locations, while the resistive polarization represents ohmic losses. As the losses increase with current, the initially increasing power finally begins to decrease, so that power maxima emerge (Fig. 3).

The voltage equation used in [14] for the purpose of the power calculation is
:

$$V = E_0(T, p_{H_2}) - iA_R(p_{H_2})\exp\left(\frac{\Delta E}{RT}\right) + B\ln\left(1 - \frac{i}{i_L(T, p_{H_2})}\right) \quad , \tag{30}$$

where a limiting current is introduced defined by an equation

$$i_L = C_1 T^{-1} \exp(\frac{-E_a}{RT}) p_{H_2} \tag{31}$$

in which C_1 is a experimentally determined parameter. Power density is simply the product of voltage V and current density i. In an ideal situation (no losses) the cell voltage is defined by the Nernst equation. Yet, while the first term of Eq. (30) defines the voltage without load, it nonetheless takes into account losses of the idle run, which are the effect of flaws in electrode constructions and other imperfections which cause that the open circuit voltage will in reality be lower than the theoretical value. Activation polarization V_{act} is neglected in this model. The losses include ohmic and concentration polarization. The second term of Eq. (30) quantifies ohmic losses associated with electric resistance of electrodes and flow resistance of ions through the electrolyte. The third term refers to mass transport losses. Quantity i_L is the current arising when the fuel is consumed in the reaction with the maximum possible feed rate.

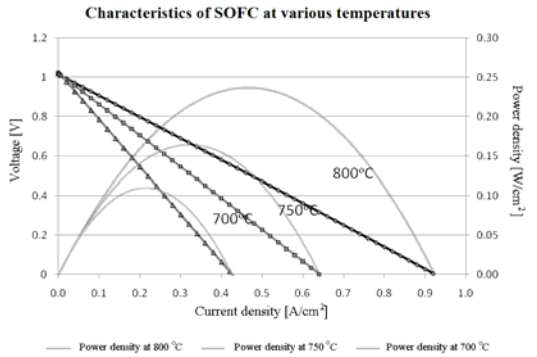

Fig.3. Voltage-current density and power-current density characteristics of the SOFC for various temperatures. Continuous lines represent the Aspen Plus™ calculations testing the model consistency with the experiments. These lines were obtained in Wierzbicki's MsD thesis supervised by S. Sieniutycz and J. Jewulski [14]. Points refer to experiments of Wierzbicki and Jewulski in Warsaw Institute of Energetics ([14] and ref [18] therein).

In the literature there are many experimental and theoretical examples showing power maxima in fuel cells and proving the suitability of the theory to chemical and electrochemical systems. For example, data obtained in L. Chen's research group [15] are consistent with those of Wierzbicki [14].

10 Concluding Remarks

This research provides data for power production bounds (limits) which are enhanced in comparison with those predicted by the classical thermodynamics. When infinite reservoirs assure constancy of chemical potentials, problems of extremum power are static optimization problems. For finite reservoirs, however, amount and chemical potential of an active reactant decrease in time, and considered problems are those of dynamic optimization and variational calculus. In fact, thermostatic bounds are often too far

from reality to be really useful. Generalized bounds, obtained here by solving HJB equations, are stronger than those of thermostatics. As opposed to classical thermodynamics, they depend not only on state changes but also on irreversibilities, ratios of stream flows, stream directions, and mechanism of all transfers. The methodology familiar for thermal machines can be applied to electrochemical engines. Extensions are available for multicomponent, multireaction chemical systems [11]).

A real work supply can only be larger than the finite-rate bound obtained by the optimization. Similarly, the real work delivered from a nonequilibrium work-producing system (with the same boundary states and duration but with a suboptimal control) can only be lower than the corresponding finite-rate bound. Indeed, the two bounds, for a process and its inverse, which coincide in thermostatics, diverge in thermodynamics. With thermokinetic models, we can confront and surmount the limitations of applying classical thermodynamic bounds to real processes.

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