Basic Thermodynamic Properties of Fuel Cell Systems

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In this work we study thermodynamics of power yield and power limits in electrochemical systems of fuel cell type. Power maximization approach is applied for SOFC treated as flow engines driven by chemical reagents and electrochemical mechanism of electric current generation. Performance curves of a SOFC system are analyzed. Steady-state model of a high-temperature cell is considered, which refers to constant chemical potentials of incoming hydrogen fuel and oxidant. Lowering of the cell voltage below its reversible value is attributed to polarizations and imperfect conversions of reactions. Power formula describes the effect of efficiency, transport laws and polarizations. It is shown how reversible electrochemical theory is extended to the case with dissipative chemical reactions; this case includes systems with incomplete conversions, "reduced affinities" and an idle run voltage. Efficiency lowering is linked with polarizations (activation, concentration and ohmic). Effect of incomplete conversions is modeled by assuming that substrates can be remained after the reaction and that side reactions may occur. Optimum conditions are found for basic input parameters. Power data differ for power generated and consumed, and depend on system's characteristics, e.g., current intensity, number of mass transfer units, polarizations, electrode area, etc.. They provide bounds for FC generators, which are more exact and informative than reversible bounds for electrochemical transformation.

1. Introduction

In a previous work (Sieniutycz and Kubiak, 2002) we modeled power production and its limits in purely thermal systems with finite rates. In particular, radiation engines were analyzed as nonlinear systems governed by laws of thermodynamics and transport (Sieniutycz and Kuran, 2006). Temperatures T of resource media were only necessary variables to describe these systems. However, fuel cells are more general systems in which both temperatures T and chemical potentials μ_k are essential.

Fuel cells (FC) are electrochemical engines propelled by fluxes of both energy and substances (Zhao *et al.*, 2008). Their role for environmental protection cannot be underestimated. The main advantage of fuel cells in comparison to heat engines is that their efficiency is not a major function of device size. A fuel cell transforms a part of chemical energy into electrical energy by consuming fuel and oxidant. In the present paper power maximization approach is applied for the purpose of determining power limits in imperfect fuel cells, where power decreases with current for sufficiently large electric currents because of prevailing effect of loss phenomena. The beginning of this approach was published by Sieniutycz (2005).

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 continuously to the cathode (positive electrode) compartment. Electrochemical reactions take place at the electrodes to produce an electric current. Basic reaction is the electrochemical oxidation of fuel, usually hydrogen, and the reduction of the oxidant, usually oxygen. This principle makes a fuel cell similar to a chemical engine. In a FC process in Fig. 1 streams of fuel (H_2) and oxidant (O_2) interact; the process is propelled by diffusive and/or convective fluxes of heat and mass, transferred through various cell 'conductances' or boundary layers. Energy flux (power) created in the cell exploits the fuel stream contacting with the anode and the oxidant stream contacting with the cathode. Both electrodes are separated by the electrolyte. As in thermal machines and radiation engines both transfer mechanisms and properties of conducting layers influence the rate of power production.
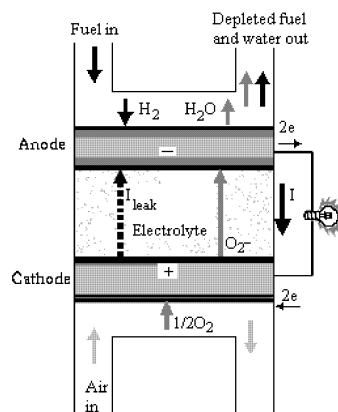

Figure 1. Principle of a solid oxide fuel cell

The goals of this work include: (a) formulation of a thermo-electro-chemical model for imperfect cells, especially for those with incomplete chemical conversions, (b) model implementation to simulate behavior of high-temperature SOFCs, (c) prediction of various voltage losses and their effect on the cell performance, and, (d) application of fuel cell characteristics and theoretical analysis to determine power limits (Sec.4).

2. Thermodynamics of power yield

Knowing operational voltage one can define a cell efficiency as the ratio $\chi = V/E$, where E is the reversible cell voltage. For power density in terms of χ one has $p=iE\chi$ or $p=\chi p^{rev}$, which means that the efficiency equals the ratio of actual power to maximum reversible power. This definition links fuel cell efficiency with the second law, and stresses a substantial role of the operational voltage.

Assume that all incoming streams (those with "higher" input of Gibbs flux $G_{in} = G_{1'}$) represent a common phase of "substrates" (all system's components in the state before the chemical transformation, index 1'). All outgoing streams (those with "lower" Gibbs

flux $G_{out} = G_{2'}$) represent a common phase of "products" (all system components in the state after the transformation, index 2'). Power p follows from entropy conservation and energy balance in the reversible part of the system. For an isothermal reactor

$$p = \mu_{1_{1'}}\dot{n}_{1_{1'}} + \mu_{2_{1'}}\dot{n}_{2_{1'}} + ... \mu_{i_{1'}}\dot{n}_{i_{1'}} .... + \mu_{m_{1'}}\dot{n}_{m_{1'}} - \mu_{1_{2'}}\dot{n}_{1_{2'}} - \mu_{2_{2'}}\dot{n}_{2_{2'}} .... - \mu_{i_{2'}}\dot{n}_{i_{2'}} .... - \mu_{m_{2'}}\dot{n}_{m_{2'}} \tag{1}$$

This formula shows that, in a steady and isothermal process, power yield of a chemical engine system is the difference between the input and output flux of the Gibb's function (Zhao *et al.* 2008). Specializing to the important case of a complete conversion, we can transform Eq, (1) to a pronouncing form of Eq. (2) below. In this case components are numbered such that species 1,2 ...*i* are substrates and species i+1, i+2 ...*m* are products. Total power yield of an isothermal multi-reaction process takes then the form

$$p = \sum_{j=1}^{R}\{p_j\} = \sum_{j=1}^{R} -\{\mu_{1_{2'}}v_{1j} + \mu_{2_{2'}}v_{2j} + ... \mu_{i_{2'}}v_{ij} + \mu_{i+1_{2'}}v_{i+1j} + . \mu_{m-1_{2'}}v_{m-1j} .. + \mu_{m_{2'}}v_{mj})\}\dot{n}_j \tag{2}$$

Quantities $\dot{n}_j$ are molar chemical fluxes of reagents, i.e. products of the electrode surface area F and heterogeneous rates, r_j. For a complete conversion, power yield from the electrode unit area equals the sum of products of affinities and reaction rates

$$p = \sum_{j=1}^{R}\{\tilde{A}_j\dot{n}_j\} = F\sum_{j=1}^{R}\{\tilde{A}_jr_j\} \tag{3}$$

Yet, the assumption about a complete transformation of substrates into products can be too restrictive, so the present paper shows how the assumption can be relaxed. By considering chemistry of systems with power production and transport phenomena one can quantitatively estimate effects of incomplete conversions (Sieniutycz, 2009). For a single isothermal reaction a power formula which generalizes Eq. (3) to include effect of incomplete conversions can be written in the form

$$p = (\Pi_{1'} - \Xi\Pi_{2'})\dot{n}_{1'} = -\frac{iA}{n_eF}\Delta g^{eff}(T,p) = -\Delta\dot{G}^{eff} \tag{4}$$

where primed quantities refer to inputs and outputs of the chemically active zone and $\dot{Q}_{1'}$ is total heat flux (involving sensible heat flux, $q_{1'}$, and the sum of products of partial entropies and fluxes of species multiplied by temperature T). $\Pi_{1'}$ is "one-way chemical affinity" attributed to reactants with known chemical potentials, and $\dot{n}_{1'}$ is the (positive) chemical flux defined as the product of heterogeneous reaction rate and electrode area. Incomplete conversion is described by the fraction Ξ which is, in fact, the reciprocity of coefficient Ψ introduced earlier by Sieniutycz (2009). Both quantities, Ξ and Ψ, characterize detrimental increase of chemical potentials of reaction products caused by their dilution by remaining reactants. Equation (4) generalizes the idealized power of an "endoreversible" system ($\Xi=1$) in which case the potential difference $\Pi_{1'} - \Pi_{2'}$ is chemical affinity or $-\Delta g$. In fact, the equation describes chemical component of power caused by chemical flux $n_{1'}$. Power is generated with non-ideal chemical efficiency $\xi = \Pi_{1'} - \Xi\Pi_{2'}$. For the simplest reaction, $1 \Leftrightarrow 2$, $\xi = \mu_{1'} - \Xi\mu_2$ which is lower

than $\mu_{1'} - \mu_{2'}$. Effectively, in the engine mode where $\Xi = <1$, a system with internal imperfections behalves as it would operate with a decreased affinity of an effective value $\Pi_{1'} - \Xi \Pi_{2'}$. Of course, power production is decreased by this imperfection.

3. Effect of transport phenomena

Transported energy and components drive power generation in chemical engines and fuel cells. Interestingly, there exists a formal link between the mathematics of thermal engines and fuel cells. (For brevity we limit the chemistry to the case of a simple isomerisation reaction A_1-$A_2 = 0$.) To show this link let us note that the active (power producing) force in an endoreversible thermal engine equals $T_{1'} - T_{2'}$. Whereas the propelling force in the simplest chemical engine is $\mu_{1'} - \mu_{2'}$. For bulks of streams or reservoirs the related differences of temperature and chemical potential are $T_1 - T_2$ and $\mu_1 - \mu_2$. Since the deviations of $T_{1'}$ and $\mu_{1'}$ from T_1 and μ_1 are of purely dissipative origin and the bulk differences $T_1 - T_2$, and $\mu_1 - \mu_2$ are identical with the "open circuit" (Carnot) values for the "active" differences $T_{1'} - T_{2'}$ and $\mu_{1'} - \mu_{2'}$, we may write

$$T_{1'} - T_{2'} = T_1 - T_2 - I_s(R_{1s} + R_{2s}) \tag{5}$$

$$\mu_{1'} - \mu_{2'} = \mu_1 - \mu_2 - I_n(R_{1n} + R_{2n}), \tag{6}$$

where I_s and I_n are the conserved currents of entropy and mass flowing through the energy-generating zone of the system. Indices 1 and 2 refer, respectively, to the resistances in the "upper" and "lower" part of the engine system. Active (power producing) driving forces, corresponding with Eqs. (5) and (6), are temperature difference $T_{1'} - T_{2'}$ and chemical affinity $\mu_{1'} - \mu_{2'}$. Total power yield is

$$p = (T_{1'} - T_{2'})I_s + (\mu_{1'} - \mu_{2'})I_n$$
$$= (T_1 - T_2)I_s + (\mu_1 - \mu_2)I_n - (R_{1s} + R_{2s})I_s^2 - (R_{1n} + R_{2n})I_n^2 \tag{7}$$

In terms of the definitions of total resistances and applied to the case of a coupled heat and mass transfer, Eq. (7) can be written in a generalized form

$$p = (T_{1'} - T_{2'})I_s + (\mu_{1'} - \mu_{2'})I_n$$
$$= (T_1 - T_2)I_s + (\mu_1 - \mu_2)I_n - R_{ss}I_s^2 - R_{ss}I_sI_n - R_{nn}I_n^2 \tag{8}$$

Let us now extend our reasoning to generalize formula (8) to fuel cells described by the formalism of inert components (Sundheim, 1964) rather than the ionic description (Newman, 1973). In this case vector of active (power producing) driving forces involve: temperature difference $T_{1'} - T_{2'}$, chemical affinity $\mu_{1'} - \mu_{2'}$ and operating voltage $\phi_{1'} - \phi_{2'}$. Total power yield is the sum of thermal, substantial and electric components, i.e.

$$p = (T_{1'} - T_{2'})I_s + (\mu_{1'} - \mu_{2'})I_n + (\phi_{1'} - \phi_{2'})I_e = (T_1 - T_2)I_s + (\mu_1 - \mu_2)I_n + (\phi_1 - \phi_2)I_e$$
$$- R_{ss}I_s^2 - R_{nn}I_n^2 - R_{ee}I_e^2 - R_{sn}I_sI_n - R_{se}I_sI_e - R_{ne}I_nI_e \tag{9}$$

After introducing the enlarged vector of all driving potentials $\tilde{\mu} = (T, \mu, V)$, flux vector $\tilde{\mathbf{I}}$ = of all currents (I_s, I_n, I_e), and the overall resistance tensor $\tilde{\mathbf{R}}$, Eq. (9) can be written in a simple and concise matrix-vector form

$$p = (\tilde{\mu}_1 - \tilde{\mu}_2).\tilde{\mathbf{I}} - \tilde{\mathbf{R}} : \tilde{\mathbf{I}}\tilde{\mathbf{I}} \tag{10}$$

4. Power limits in thermal power systems and fuel cells

While the dimensionality of the potential vector $\tilde{\mu}$ can occasionally be much larger in real systems, the structure of Eq. (10) may still be preserved for the related vector form. Maximum power corresponds with the vanishing partial derivatives

$$\partial p / \partial \tilde{\mathbf{I}} = \tilde{\mu}_1 - \tilde{\mu}_2 - 2\tilde{\mathbf{R}}.\tilde{\mathbf{I}} = 0. \tag{11}$$

Therefore, the optimal (power-maximizing) vector of currents at the maximum point of the system can be written in the form

$$\tilde{\mathbf{I}}_{mp} = \frac{1}{2}\tilde{\mathbf{R}}^{-1}.(\tilde{\mu}_1 - \tilde{\mu}_2) \equiv \frac{1}{2}\tilde{\mathbf{I}}_F \tag{12}$$

This result means that in the strictly linear systems the power-maximizing current vector $\tilde{\mathbf{I}}_{mp}$ is equal to one half of the purely dissipative current at the Fourier-Onsager point, $\tilde{\mathbf{I}}_{mp}$. The latter point refers to the system's state at which no power production occurs. Consistently, Eqs. (10) and (12) yield the limiting power

$$p_{mp} = \frac{1}{4}\tilde{\mathbf{R}} : \tilde{\mathbf{I}}_F\tilde{\mathbf{I}}_F \tag{13}$$

On the other hand, power dissipated at the Fourier-Onsager point equals $p_F = \tilde{\mathbf{R}} : \tilde{\mathbf{I}}_F\tilde{\mathbf{I}}_F$. Therefore, our analysis proves that, in linear thermo-electro-chemical systems, only at most 25% of power dissipated in the natural transfer process, can be transformed into the noble form of the mechanical power. This is a general conclusion which, probably, cannot easily be generalized to the nonlinear transfer systems where significant deviations from Eq. (13) may depend on the nature of diverse nonlinearities. In addition, our analysis shows that thermal force formulae and power formulae for thermal engines are similar to the voltage and power formulae in a fuel cell system. This observation proves that a link exists between the mathematics of thermal engines and fuel cells, and also that the theory of fuel cells can be unified with the theory of thermal engines.

5. Summary remarks

The FC model developed in this paper describes performance of fuel cells at various operating conditions. Lowering of SOFC efficiency is linked with polarizations (activation, concentration and ohmic) and incomplete conversions. Effect of incomplete

conversion has been modelled assuming that substrates can be remained after the reaction and that side reactions may occur. Power limits have been obtained for fuel cells in terms of parameters such as efficiency, resource input, and electric current density. Calculations show that the power data differ for power generated and consumed, and depend on parameters of the system, e.g., current intensity, number of mass transfer units, polarizations, electrode surface area, average chemical rate, etc.. These data constitute bounds for SOFC energy generators, which are more exact and informative than the reversible bounds well known for electrochemical transformations. A recent publication (Sieniutycz 2011) shows an example of numerical results of the new implementation on the cell performance along with the discussion of the relevant literature. In fact, the new formulation improves the numerical prediction of various voltage losses and their effect on the cell performance, and the application of fuel cell to determine power limits.

Acknowledgments

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