Conditions for Autonomy of a DMFC System

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1   Motivation

Methanol-powered fuel-cell systems have a great potential for portable power in comparison to today's ubiquitous lithium-ion batteries: the energy density of methanol is over 15 times that of Li-ion batteries on volume basis, and over 40 times on mass basis (Li-ion energy densities: ~1 J/mm³ and ~0.5 J/mg (Tarascon and Armand, 2001). Methanol energy densities: 17.36 J/mm³ and 21.92 J/mg (Perry and Green, 1997)).

Direct methanol fuel cells (DMFC) convert methanol directly into electricity; while the overall efficiency of present systems may not be impressive (~20%), the high energy density of methanol more than offsets these losses.

Compared to a Li-ion battery pack, a DMFC system requires a "dead weight" to process methanol into electricity, i.e. the fuel-cell stack itself, separators, mixers and coolers. Therefore, DMFC, compared to Li-ion batteries, have more of an advantage at low power-to-energy ratios, i.e. for applications required to run independently for a long time.

DMFC systems are already available in fire-surveillance cameras, as mobile power supply for recreational vehicles, and portable power supply for military applications.
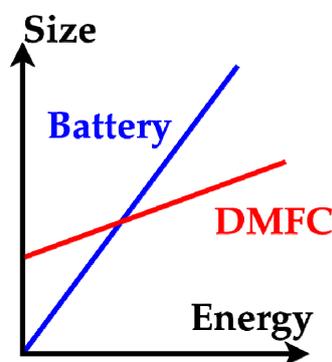

Figure 1:   Energy density of DMFCs and batteries.

2   DMFC Reference System

DMFC systems can be divided up in two groups: *passive* systems, in which reactant transport is obtained by physical phenomena such as capillary pressure (Zhao et al., 2009), and *active* systems, in which the flows are driven by pumps, blowers or compressors.

Active systems are more flexible, can react better to changing environmental conditions and are more efficient, but require a larger dead weight for their ancillary units; therefore, passive systems are preferred for smaller-size applications such as mobile phones, whereas active systems are more appropriate for laptop computers or portable power sources.

The modelled system is an active one, in which all units perform a single task without any integration (the exception being the fuel-cell stack itself). The system operates at atmospheric pressure, and is referred to as the *reference* system.

The stack's anodic side operates on a lean methanol solution (~1M), pumped from a mixing tank. The solution is cooled after passing through the stack and the carbon dioxide produced by the reaction is then separated. The liquid phase returns to the mixer, completing the *anodic loop*. The stack's cathodic side is fed by environment air, which is pushed through the system by an inlet blower. The cathodic outlet is then cooled by a heat exchanger and any condensed water is recovered to the mixer. The neat methanol is pumped directly into the mixer.
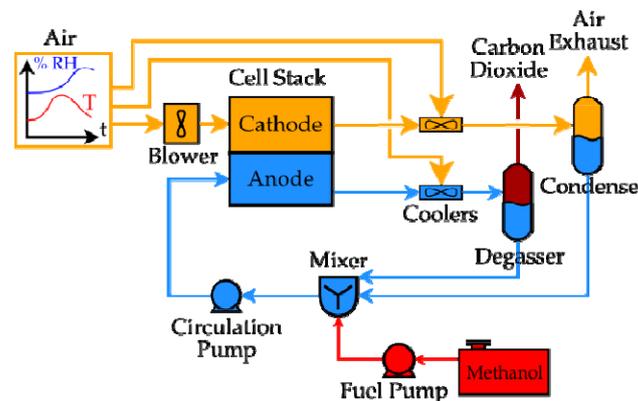

Figure 2:   The reference DMFC system.

The fuel-cell stack includes several phenomena, the most important of which are:

- The anodic reaction, in which methanol and water are consumed to produce protons, electrons and waste carbon dioxide;
- The cathodic reaction, in which protons, electrons and oxygen produce water;
- The methanol cross-over, caused by diffusion of methanol through the membrane;
- The water drag, caused by the hydration of protons migrating to the cathode;
- Voltage is not modelled in full detail, but rather with a Thévenin approximation (i.e. voltage generator and a resistance), which is more appropriate for our purposes.

Separators perform an ideal separation of two phases. Coolers are assumed to be controlled so that it is possible to set their process outlet temperature, within physical bounds. The mixer is the only unit with a mass hold-up, since it is assumed to store a much larger quantity of solution than all other units. Both the fuel-cell stack and the mixer have an energy hold-up, though the stack considers only the heat capacity of the plates.

The resulting dynamic model is appropriate for bandwidths in the order of magnitude of several minutes or slower.

3   Dynamics and Control of DMFC Systems

The system model described in the previous section has been analysed for stability and controllability. The main dynamic variables are that of solution volume, methanol con-

centration, mixer temperature in the anodic loop, oxygen partial pressure in the cathode, and fuel-cell temperature.

All dynamic modes are stable, with the important exception of solution volume, which is *metastable* and slowly drifts away from its nominal value. Simulations indicate that this reduction can be as slow as 1 cm^3 every several hours for portable systems, which makes the issue difficult to notice in laboratory test runs. To make a commercial system viable, however, solution volume must be controlled so that it is maintained to an acceptable value: to control a metastable dynamics, feedback control and some measurement of solution volume are mandatory.

The adopted control strategy was to use a set of single-input, single-output controllers (decoupled control), with one controller for each dynamics. The resulting layout included (Zenith and Krewer, 2010):

- Feedforward stoichiometry (λ) control for both cathode and anode inflow;
- Feedback PI control of the anodic cooler to set stack temperature;
- Feedback P control, with gain scheduling, of the cathodic cooler to stabilise the solution volume;
- Feedforward control of neat-methanol inflow to the mixer, to compensate consumption by reaction and cross-over.

The simulations and experimental runs indicated that the overall control system is sound, and that interactions among the control loops are limited; the only significant one, which is the interaction between the control loops of stack temperature and methanol concentration, does not lead to instability under broad conditions.

4   Autonomy and Feasibility Envelope

Given that it is possible to control a DMFC system such as the proposed one, it remains to be seen in which conditions this is at all feasible. The most critical variable is the water content in the solution: water is removed from the anodic side of the stack, mostly by the electro-osmotic drag, and must be recovered by the condenser on the cathodic side. The ability of a DMFC system to maintain its water content is termed *autonomy*.

Since the minimum achievable condenser temperature is limited by the environment temperature, it can be imagined that there are conditions in which it will not be possible to recover the necessary amount of water if environment temperature is too high.

Indeed, a steady-state analysis based on material balances shows that the autonomy of a DMFC system depends on a surprisingly small set of variables (Zenith et al., 2010):

- Cathodic reactant excess ratio (the cathodic λ);
- Environmental humidity;
- Condenser temperature.

It is worth remarking that autonomy does not depend on any of the following:

- Current, voltage or other electrochemical variables;
- Concentration, stack temperature, anodic flow rate, or other operating conditions;
- Any cell parameter, such as those describing methanol cross-over, electro-osmotic drag, number or size of cells.

Autonomy of DMFC systems can therefore be determined in very general terms, for any DMFC system configured as our reference system (or systems with different configuration but leading to the same mass balances). One solution of the autonomy relationship is presented in figure 3.
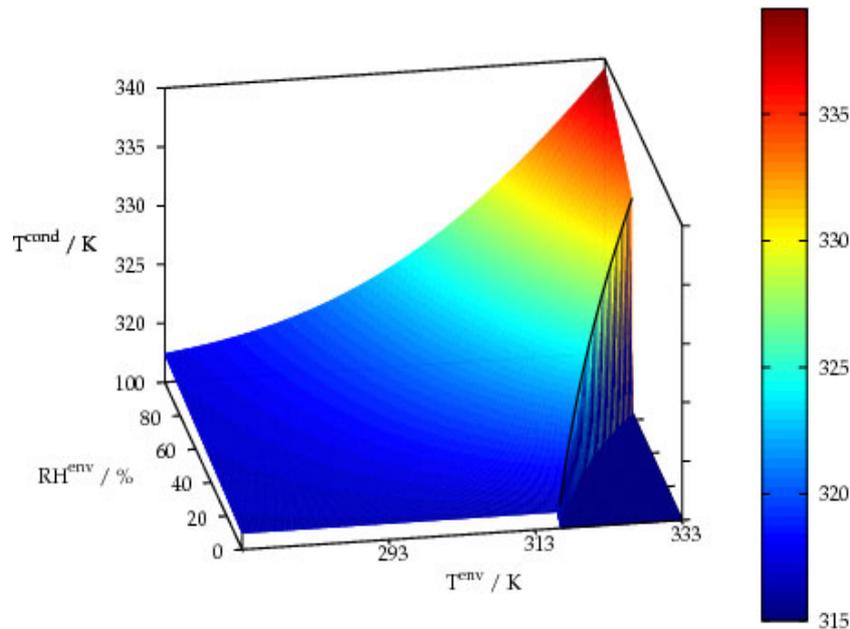

Figure 3:   The value of T^{cond} represents the autonomy relationship; the sharp drop on the right is the edge of the feasibility envelope. The plot is for $\lambda = 3$.

The set of environmental conditions (humidity and temperature) allowing operation of DMFC systems is termed the *feasibility envelope*. If necessary, this envelope can be extended by diluting the methanol reservoir with water, an approach taken in some prototypes produced by the industry; calculations, however, show that this approach does not improve autonomy significantly, and has the price of reducing the DMFC's main advantage, i.e. energy density.

Extending the envelope by means of system pressurisation seems a more promising approach, even though pressurisation is known to reduce system efficiency and should be avoided whenever possible. Specularly, operation at pressures lower than one standard atmosphere (for example in high altitude) results in a significantly tighter feasibility envelope.

5   Determination of Cross-Over Parameters

The proposed DMFC system contains three feedforward control systems to set cathodic, anodic, and neat-methanol inflows. The autonomy criterion was derived assuming this control is perfectly implemented. All these feedforward control laws have to compensate for the cross-over, whose estimation is therefore of critical importance.

To estimate the cross-over, the system was run on a slightly modified configuration: the neat methanol was injected directly on-line between the mixer and the fuel cell, and the concentration downstream of the mixing point was measured by a sensor. The neat-methanol inflow was then set by a PI feedback controller, that maintained an inlet concentration of 1 M with a standard deviation of 2.5%.

Maintaining the stack temperature at 60 °C and the anodic cooler's at 40 °C, the cross-over was estimated by setting several currents in the interval between open circuit and 2300 A/m^2 and measuring the inflow of neat methanol set by the concentration feedback controller. When the steady state is reached, the resulting neat-methanol inflow is the steady-state sum of methanol lost to anodic reaction, cross-over and anodic separator (the last one being a negligible term).

The cross-over model was validated by nonlinear model fitting. The two parameters used to estimate cross-over could be estimated with good precision, indicating that feedforward control is realistic.

The two parameters are the mass-transport coefficients from the anodic bulk to the membrane (k_m) and from the anodic side of the membrane to the cathodic one (k_x), the latter being relevant for crossed-over methanol only.

Table 1:   Estimates for mass-transport coefficients at 60°C, 1 M.

Parameters	Estimation	Standard deviation
k_m	8.00 µm/s	2.3 %
k_x	1.98 µm/s	1.8 %

In further work, the cross-over will be estimated for other stack temperatures and methanol concentrations, in order to enable feed forward control in real systems, where these variables may change.

References

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