Optimal Concentration Control for Direct Methanol Fuel Cells

Federico Zenith^{*} Youngseung Na^{**,***} Ulrike Krewer^{**}

* SINTEF Applied Cybernetics, PO Box 4760 Sluppen, NO-7465 Trondheim, Norway (e-mail: federico.zenith@sintef.no) ** TU Braunschweig, Franz-Liszt-Straße 35, 38106 Braunschweig, Germany

*** International Max Planck Research School for Advanced Methods in Process and Systems Engineering, Sandtorstraße 1, 39106 Magdeburg, Germany

Abstract: Two modifications to a reference direct methanol fuel-cell (DMFC) system are considered to improve methanol fuel utilisation. Fuel utilisation can be optimised by minimising the parasitic methanol crossover by manipulating methanol concentration in the fuel cells. Simulations of the two systems indicate that there is considerable potential to increase fuel utilisation for dynamic concentration control in DMFC systems subject to variable load.

Keywords: Fuel cell; MIMO; feedforward; feedback; methanol; DMFC; dynamics; simulation; efficiency

1. INTRODUCTION

Fuel cells are devices able to convert the energy stored in chemical bonds into electrical DC power by means of electrochemical reactions. Differently from batteries, fuel cells are not self-contained and require a continuous flow of reactants to produce power. As long as the reactants are provided, fuel cells will produce power, and never deplete as a battery would.

Most research in fuel cells focuses on hydrogen fuel cells, often proposed as a replacement to polluting internal combustion engines (ICE) in vehicles, or as micro combined heat and power generators for domestic use. Fuel cells have in these applications the advantage of higher efficiency than current technologies (ICE, small generators), silent operation, no major moving parts, and the ability to run on hydrogen, a fuel that can be manufactured readily from any energy source.

Direct methanol fuel cells (DMFCs) are a particular type of fuel cells whose application area is instead focused more on small and portable electronics. DMFCs have the particularity of running on methanol fuel, which is liquid in all environmental conditions experienced on Earth: this makes handling of the fuel much easier than with hydrogen, which needs to be compressed at very high pressures (700 bar for recent fuel-cell electric vehicles) in order to attain an acceptable energy density.

On the other hand, DMFCs have markedly lower efficiencies than other fuel cells (about 25%), and are in that regard in fact comparable to ICEs running on methanol: therefore, DMFCs are generally not competitive for automotive applications. However, they are much more attractive in small, portable electronics, and in backup power generation, when the energy storage capacity of batteries

is insufficient.

The strong point of DMFCs is the high energy density of methanol, theoretically about 30–40 times that of Liion batteries: even accounting for the low efficiency of DMFCs, methanol's net energy density is still about 10 times higher. While the efficiency of DMFCs is much lower compared to batteries, this is not necessarily an issue in portable applications: what is much more important to end users is for how long time their electronic devices can operate.

However, even if efficiency is not the primary concern, it is still a factor in determining the amount of energy the DMFC is able to deliver: any increase in efficiency will directly result in a proportional increase in delivered DC power, and thereby operational time of the electronic device.

Since about 75% of the energy available in methanol is wasted to heat in DMFCs, it is very interesting to investigate ways to recover some of this energy by increasing their conversion efficiency. Arisetty et al. (2009) demonstrated experimentally that for every power level produced by a DMFC there is an optimal methanol concentration in the anodic solution that results in a maximum voltage, corresponding to a maximum efficiency of electrochemical conversion.

This paper proposes two modified system layouts derived from a previously published reference system (Zenith and Krewer, 2010) with adapted control approaches to maximise fuel utilisation, and evaluates their potential.





2. METHODS

2.1 The Reference DMFC System

A generic DMFC system is sketched in Figure 1; this system is indicated as the *reference* since it represents a convenient reference point for process modifications proposed in this paper. In the reference system, all ancillary units perform a single conceptual task: separators divide gas and liquid flows, heat exchangers set an outlet temperature, pumps and blowers set specific gas or liquid flows, and the mixer accumulates liquids.

The reference system has previously been studied, in particular with the objective of controllability analysis and control synthesis (Zenith and Krewer, 2010); only the more relevant results will be summarised in this section.

In the reference system of Figure 1, a diluted methanol solution enters the anodic side, whereas air enters the fuel cell stack from the cathodic side; the electrochemical reactions are, on anode and cathode respectively:

$$CH_3OH + H_2O \longrightarrow 6H^+ + 6e^- + CO_2\uparrow$$
 (1)

$$\frac{3}{2}O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O$$
⁽²⁾

Protons H^+ pass through the membrane separating anode and cathode, whereas electrons e^- pass through the external circuit and provide DC power to the fuel cell's load.

The neat methanol contained in the storage tank is diluted in water before being sent to the anode at relatively low concentrations, typically about 1 M. The reason is only partly that equation 1 requires the presence of water, since two other phenomena must be considered:

- Electro-osmotic drag: every H⁺ passing through the membrane will drag along with it about 4 molecules of water;
- Methanol crossover: methanol can diffuse through the membrane, and react on the cathodic side; low methanol concentrations minimise this effect.

In practice, electro-osmotic drag is the main driver removing water from the anodic loop and bringing it to the cathode; therefore, the cathodic outlet is cooled and water is recovered in a separator to maintain the amount of water in the anodic loop without external supply of make-up water.

Fig. 2. Schematic diagram of methanol reactions in a DMFC, both main reaction and crossover.

2.2 Methanol Crossover

Methanol crossover occurs because any methanol that reaches the cathodic side of the cell will instantaneously react with oxygen: there is therefore always a concentration gradient between cathode, where concentration is zero, and anode, where concentration must be larger than zero for reaction 1 to occur. This concentration gradient is the driving force of methanol crossover.

Methanol crossover is a crucial phenomenon for DMFC efficiency, reducing it in two ways:

- (1) By subtracting methanol from reaction 1;
- (2) By reacting methanol on the cathode and increasing cathodic overvoltage, reducing the overall cell voltage and with it the electrochemical conversion efficiency.

The already cited Arisetty et al. (2009) studied the latter phenomenon, since they focused on the voltage produced by a cell. It is, however, difficult to come to general conclusions in a simulation study about that aspect, since cell voltage depends on many factors, and the exact effect of methanol crossover on voltage can change with each cell. This paper focuses therefore on the former phenomenon, which can be more readily quantified and treated by simulation. Obviously, any implementation of the control solutions proposed in this paper will need to be calibrated to take into account the influence of voltage.

It was shown that crossover can be modelled quite accurately with a simple lumped-parameter model (Zenith and Krewer, 2011). In this model, illustrated in Figure 2, methanol has a uniform concentration c in the anode bulk, which is reduced due to diffusion to the catalystlayer concentration c_{cl} . At the catalyst layer, part of the methanol reacts in main reaction 1, and part proceeds across the membrane to the cathode, where concentration falls to zero.

2.3 Modified Systems for Fast Concentration Control

In the reference system of Figure 1, concentration control relies on a feedforward strategy, made possible because methanol crossover has a stabilising effect: as crossover losses decrease with low concentrations and increase with high concentrations, a stable concentration is eventually reached; this effect was first noticed experimentally by Ha et al. (2008).



Fig. 3. The new proposed DMFC system layout with an inline methanol mixer, placed after the main circulation pump.



Fig. 4. The new proposed DMFC system layout with an inline methanol mixer and separate tank for recovered water.

By estimating crossover losses, it is possible to implement a feedforward controller able to maintain concentration within a standard deviation of 8% (Zenith and Krewer, 2011). However, this control strategy is slow to react to changes in the set point for concentration, since all concentration transients are dampened by the relatively large solution holdup of the mixer (see Figure 1).

The feedforward concentration controller proposed in Zenith and Krewer (2011) is therefore best suited for constant set points in concentration; but, for systems operating with rapidly changing power production levels, such as a laptop PC, the ability to rapidly change methanol concentration could significantly boost efficiency.

Two alternative systems are proposed to improve the controllability of concentration: a system with an inline mixing of neat methanol, such as in Figure 3; and another system with inline mixing, but with the further modification of having a second tank for recovered water from the cathode outlet, as in Figure 4.

The objective of both system modifications is to rapidly set the fuel cells' inlet concentration by mixing the spent solution with methanol (and water, in the second layout), thereby generating the requested solution on-the-fly.

Copyright © 2015 IFAC

2.4 Control of the Modified DMFC Systems

Control of the DMFC systems of Figures 3 and 4 is synthesised as a modification of the control system proposed for the original reference system of Figure 1 in Zenith and Krewer (2010).

Estimation of Methanol Concentration in Solution Tank Controllers will need an estimate of the concentration in the solution tank, assuming no on-line measurements are to be installed. This is possible thanks to the stability of the concentration dynamics.

Assuming there is a way to measure or infer the volume V^{sol} of liquid in the tank in which the solution is, the differential equation describing the amount of moles in the anodic loop is:

$$\frac{\mathrm{d}\tilde{n}_{\mathrm{CH}_{3}\mathrm{OH}}^{\mathrm{sol}}}{\mathrm{d}t} = \frac{\rho_{\mathrm{CH}_{3}\mathrm{OH}}}{M_{\mathrm{CH}_{3}\mathrm{OH}}} \dot{V}^{\mathrm{fuel}} - \tilde{r} - \tilde{d}$$
(3)

where n is the number of moles, ρ is density, and M is the molar mass; the tilde (~) indicates an estimate. \tilde{r} is the estimated reaction rate (for anodic reaction 1 and crossover) and \tilde{d} is the methanol loss in the degasser; both are in mol/s and can be estimated reliably.

Concentration is then estimated as $\tilde{c}^{\rm sol} = \tilde{n}_{\rm CH_3OH}^{\rm sol}/V^{\rm sol}$, where $V^{\rm sol}$ is measured.

Optimal Inlet Concentration The optimal inlet concentration is the one that produces the maximum efficiency in the electrochemical conversion of methanol to DC power.

As anticipated in section 2.2, methanol crossover reduces efficiency by 1) subtracting methanol to the anodic reaction, and 2) by reducing the cell voltage when reacting on the cathode. Increasing cell efficiency is however not the same as minimising methanol crossover: crossover can in theory be completely eliminated by setting the bulk concentration in the anode so that $c_{cl} \rightarrow 0$, but this will cause high voltage losses in the *anodic* reaction: an optimal value must be found for which the sum of anodic and cathodic losses is minimised.

As the effect of concentration on voltage has already been studied by Arisetty et al. (2009), this paper will focus on minimisation of methanol crossover.

Faradaic efficiency ε is defined as the ratio of methanol reacted on the anode, which is proportional to current, to the methanol fed to the system:

$$\varepsilon = \frac{NI}{6F} \frac{M_{\rm CH_3OH}}{\rho_{\rm CH_3OH} \dot{V}_{\rm fuel}} \tag{4}$$

where N is the number of cells in the stack, I is the current in A, F is Faraday's constant, and \dot{V} is volumetric flow.

Equation 4 is meaningful only at steady state; in dynamic simulations, it would be disturbed by transients. The following ratio of integrals over the simulation time indicates a cumulative faradaic efficiency:

$$E = \frac{N}{6F} \frac{M_{\rm CH_3OH}}{\rho_{\rm CH_3OH}} \frac{\int_0^T I \, \mathrm{d}t}{\int_0^T \dot{V}_{\rm fuel} \, \mathrm{d}t}$$
(5)

725

Faradaic efficiency ε can also be expressed as a ratio of methanol consumed in the anodic reaction and total methanol consumed by anodic reaction, crossover and degasser loss:

$$\varepsilon = \frac{\frac{I}{6F}}{\frac{I}{6F}(1-b) + c_{\text{out}}^{\text{an}} a A + d}$$
(6)

where a and b are cell parameters defined as in our previous work (Zenith and Krewer, 2011), and $c_{\text{out}}^{\text{an}}$ is the anodic outlet concentration, which determines crossover in our model. A is the electrochemically active area in a cell.

Rearranging for c_{out}^{an} :

$$c_{\rm out}^{\rm an} \approx \frac{I}{6 F} \left(\frac{1}{\varepsilon} + b - 1\right) \frac{1}{a A}$$
 (7)

where degasser loss d has been neglected, as it is a minor term.

We approximate then that the outlet concentration is related to the anodic reactant excess ratio λ and inlet concentration c_{in}^{an} as:

$$(\lambda - 1) c_{\rm in}^{\rm an} \approx \lambda c_{\rm out}^{\rm an} \tag{8}$$

which is conservative by overestimating c_{in}^{an} , since there is a significant loss of solvent in the stack through electroosmotic drag.

The optimal set point for inlet concentration is then proportional to current I, and given by:

$$\bar{c} = \frac{I}{6F} \left(\frac{1}{\varepsilon} + b - 1\right) \frac{1}{aA} \frac{\lambda}{\lambda - 1} \tag{9}$$

where the bar (⁻) indicates a set point. The value for ε must be less than 1, because no crossover implies no methanol at the anodic catalyst layer ($c_{cl} = 0$ in Figure 2): this would however not only completely stop crossover, but also the desired anodic reaction 1, which requires methanol. In this paper, we target $\varepsilon = 95 \%$.

Control Rules for Inline-Mixer System Comparing the system of Figure 3 with the reference system of Figure 1, we have simply changed the point in which the flow of neat methanol entered the anodic loop: instead of entering a mixer tank, it is mixed online with the methanol solution just before entering the fuel cells.

In the reference system, the fuel pump sets \dot{V}^{fuel} to compensate for methanol consumption (anodic reaction, measured, and crossover, estimated), whereas the circulation pump maintains a preset methanol excess ratio (λ control).

In the new system with inline mixing, the tasks of these two variables are:

- Maintain λ control;
- Set the inlet anodic concentration c_{in}^{an} to a specific value \bar{c} , given by equation 9.

Since both flows carry methanol, they need to coordinate to attain these objectives.

To enforce λ control, the rule is:

$$\bar{c}\left(\dot{V}^{\text{fuel}} + \dot{V}^{\text{sol}}\right) = \lambda\,\tilde{r}\tag{10}$$

where reaction rate \tilde{r} is estimated from anodic reaction and crossover.

For inlet concentration control, only if $\bar{c} > \tilde{c}^{sol}$, which is most of the time:

Copyright © 2015 IFAC

$$\bar{c}\left(\dot{V}^{\text{fuel}} + \dot{V}^{\text{sol}}\right) = \tilde{c}^{\text{sol}} \dot{V}^{\text{sol}} + \frac{\rho_{\text{CH}_3\text{OH}}}{M_{\text{CH}_3\text{OH}}} \dot{V}^{\text{fuel}} \qquad(11)$$

otherwise, it is simply

$$\dot{V}^{\text{fuel}} = 0 \tag{12}$$

since no pump flow can be negative.

Assuming that an estimate of \tilde{c}^{sol} is available, as previously described, the given rules are a linear system of two equations with two unknowns, which can therefore be uniquely solved. The proposed controller is therefore a MIMO feedforward controller.

Control Rules for Separate-Tank System In the separatetank system of Figure 4, we have added a further degree of freedom by gathering recovered water in its own tank and adding a new pump for recovered water; the purpose is to be able to set inlet anode concentration to values lower than \tilde{c}^{sol} . In the inline-mixer system, if $\tilde{c}^{\text{sol}} > \bar{c}$ the fuel flow is simply set to zero, waiting for methanol depletion to run its course; in this layout, concentration can be rapidly set to any value.

The presence of two liquid tanks implies an extra state to control. In the reference and inline-mixer systems, the level of the solution tank was controlled by a P controller, regulating condensation of water from the cathode outlet (Zenith and Krewer, 2010). This controller is maintained, with the same parameters, and applied to level control of the water tank.

The task to be fulfilled by variables \dot{V}^{fuel} , \dot{V}^{sol} and \dot{V}^{water} are now:

- Maintain λ control;
- Set the inlet anodic concentration c^{an}_{in} to c̄;
 Maintain the liquid level in the solution tank.

The rule to enforce λ control is quite similar to the inlinemixer system:

$$\bar{c}\left(\dot{V}^{\text{fuel}} + \dot{V}^{\text{sol}} + \dot{V}^{\text{water}}\right) = \lambda \,\tilde{r} \tag{13}$$

To handle the remaining two tasks, it is necessary to split flows of water and fuel in two virtual components, identified by subscript $_{c}$ for concentration control and $_{V}$ for solution-tank volume control:

$$\dot{V}^{\text{water}} = \dot{V}_{c}^{\text{water}} + \dot{V}_{V}^{\text{water}} \tag{14}$$

$$\dot{V}^{\text{fuel}} = \dot{V}_c^{\text{fuel}} + \dot{V}_V^{\text{fuel}} \tag{15}$$

The rationale for this split is that the aggregated flows are constrained to be larger than zero.

Volume control for the solution tank is realised with another P controller. As the volume is measured (through e.g. pressure at tank bottom or weight of tank), it is easy to set up a controller considering that, from the point of view of \dot{V}^{water} , the total solution volume V^{sol} is an integrating process with unitary gain (i.e. one more cc from the water tank gives one more cc in total solution); also, the process is very fast as it involves only simple liquid displacement.

The solution-volume controller is therefore defined as:

$$\dot{V}_V^{\text{fuel}} + \dot{V}_V^{\text{water}} = \frac{1}{\tau_c} \left(\bar{V}^{\text{sol}} - \tilde{V}^{\text{sol}} \right) \tag{16}$$

$$\bar{c}\left(\dot{V}_{V}^{\text{fuel}} + \dot{V}_{V}^{\text{water}}\right) = \frac{\rho_{\text{CH}_{3}\text{OH}}}{M_{\text{CH}_{3}\text{OH}}} \dot{V}_{V}^{\text{fuel}}$$
(17)

726

Table 1. The current load applied to the stack in simulations.

Time	Current
0 s to 1200 s	3 A
1200 s to 1800 s	6 A
1800 s to 2400 s	3 A

Of these two equations, the first determines that the sum of flows of methanol and water is proportional to the deviation of measured solution volume $\tilde{V}^{\rm sol}$ from the set point $\bar{V}^{\rm sol}$; the second constrains the two flows to sum up to a concentration equal to \bar{c} , in order not to interfere with concentration control. Gain $1/\tau_c$ is determined according to the Skogestad SIMC rules (Skogestad, 2003), with τ_c parameter corresponding to the desired response. Since the process of liquid-volume transfer is quick, τ_c can be set to a low value, e.g. 60 seconds.

Note that the two equations presented for solution-tank volume control are valid only if $\bar{V}^{\text{sol}} > \tilde{V}^{\text{sol}}$; otherwise, it will be:

$$\dot{V}_V^{\text{fuel}} = \dot{V}_V^{\text{water}} = 0 \tag{18}$$

since flows cannot be negative.

Concentration control is realised with the rule:

$$\bar{c}\left(\dot{V}^{\text{sol}} + \dot{V}_{c}^{\text{fuel}} + \dot{V}_{c}^{\text{water}}\right) = \tilde{c}^{\text{sol}}\dot{V}^{\text{sol}} + \frac{\rho_{\text{CH}_{3}\text{OH}}}{M_{\text{CH}_{3}\text{OH}}}\dot{V}_{c}^{\text{fuel}}$$
(19)

In addition, *one* of the following equations will be valid:

$$V_c^{\text{fuer}} = 0 \qquad \text{if } \tilde{c}^{\text{sof}} > \bar{c} \qquad (20)$$

$$V_c^{\text{water}} = 0$$
 otherwise (21)

Concentration control is therefore able to set \bar{c} no matter what the current estimate of \tilde{c}^{sol} is.

The proposed controller is therefore a MIMO controller with both feedforward and feedback components.

2.5 Simulation Tools and Specification

The reference, inline-mixer and separate-tank systems were modelled in the Modelica programming language, with the same parameters their components (i.e. the only difference is the layout). The system stack consists of 20 fuel cells, each with 26 cm^2 of active area. The solution in the tank has initially a volume of 5 cm^3 and a concentration of 1 M, which are typical values for portable units. The water in the separate-tank system also starts with a volume of 5 cm^3 . The system is subject to a stepwise varying current over the course of forty minutes, as given in Table 1.

The code for these simulations is freely available for download (Zenith, since 2008).

3. RESULTS

For the three systems, the stack inlet concentrations are plotted in Figure 5, the estimated and actual concentrations in the solution tanks in Figure 6, and the volumes of solution and water in the tanks in Figure 7.

For the three simulations, the cumulated faradaic efficiency E is tabulated in Table 2.

Copyright © 2015 IFAC



Fig. 5. Concentrations for inlet anodic flow.



Fig. 6. The solution-tank concentrations for both modified layouts and their running estimated values.



Fig. 7. The volumes of solution tanks in the simulations, and of the water tank for the case of separate tanks.

Table 2. Cumulative faradaic efficiencies for the three systems with the load of Table 1.

Simulation	E
Reference system	71.5%
Inline mixer	91.8%
Separate tanks	90.6%

4. DISCUSSION

The simulations presented in the previous section indicate that all control layouts are viable alternatives able to maintain operating conditions in the DMFC system, but there are significant differences in their performance.

4.1 Analysis of Transients

The reference system has an initial increase in concentration, up to over 1.3 M, due to the lower temperatures in the first ten minutes as the stack warms up and crossover is gradually increased; otherwise, once the temperature transient settles, the inlet concentration remains stable at about 1.1 M, with minor transients when large load changes occur. The solution level in the reference system's mixer also has an initial increase, but eventually stabilises and exhibits dynamics uninfluenced by load changes.

Both modified systems experience a slow, decreasing transient in concentration for the first 20 minutes: this is because the feedforward controller is unaware that concentration is not at its steady-state level. Later transients are detected by the controller, and are promptly compensated.

The feedforward control is able to compensate very well for the changes in reference concentration after 20 minutes, but does not compensate the initial deviation because it is not aware of it. The volume of the solution tank is subject to larger oscillations than in the reference system: the degraded performance is indirectly due to the lower crossover losses, which reduce water production in the cathode, which in turn means less water can be recovered.

The system with separated tanks for spent solution and condensed water has a dynamic behaviour for concentration very similar to the inline mixer with a single tank, but its concentration control is slightly more precise. This is because of a more accurate concentration estimate, since two flows (condensed water and neat methanol) have an exactly known concentration in this layout. The volume of the solution tank is tightly controlled by the fast feedback element of the controller, but the oscillations and slow transients are simply taken over by the water tank volume. At t = 1800 s, it is visible how the controller transfers over 1 cm³ of water to the solution tank to dilute the methanol solution and follow the step change in concentration setpoint.

4.2 Analysis of Faradaic Efficiencies

In Table 2, it is evident that both new proposed layouts perform significantly better than the reference system, cutting crossover losses by about two thirds.

The system with separate tanks has a slightly lower efficiency than the one with a single tank: this is not due to its inferiority, but rather to the fact that the inlinemixer system underestimates solution-tank concentration between 1200s and 1800s much more than the separated tank, due to the previously mentioned higher precision of the latter. The higher efficiency of the inline-mixer system, therefore, is due to estimation error, and in more extreme conditions may have caused reactant starvation. Both faradaic efficiencies for the new system layouts are below the target of 95% assumed when defining the target concentration \bar{c} in equation 9. The reason for this difference is that \bar{c} has been defined without regard to methanol degasser loss d, which is small but not completely negligible.

5. CONCLUSION

Mixing methanol directly in the flow line to the fuel cell anode allows much faster concentration control and the possibility of dynamically adjusting inlet concentration to minimise crossover and maximise faradaic efficiency in DMFCs. This approach may be just as easily modified to find an optimal concentration for overall efficiency if the relationship of concentration, crossover and anodic and cathodic overvoltages is available.

In the presented example, utilisation losses were reduced by about two thirds, but the exact figure of this gain will be critically dependent on the usage pattern: a constant pattern, for example, will gain nothing from faster concentration control, while a complex, dynamic pattern may see significant improvement. Examples for former DMFC applications are power supplies for continuously operated devices, e.g. surveillance cameras; examples of the latter are portable electronics with periodic or random usage pattern, e.g. portable PCs or mobile phones.

The main advantage that justified the ideation of the separate-tank system, i.e. its ability to reduce concentration rapidly, is however of little use: as visible from Figure 6, when methanol feed is cut to zero, concentration will drop very rapidly also in the inline-mixer system, and the advantage of active dilution will be minimal.

The layout with inline mixer and single solution tank appears therefore to be a superior alternative for its simplicity, coupled with an essentially identical performance.

REFERENCES

- Arisetty, S., Jacob, C.A., Prasad, A.K., and Advani, S.G. (2009). Regulating methanol feed concentration in direct methanol fuel cells using feedback from voltage measurements. *Journal of Power Sources*, 187(2), 415– 421.
- Ha, T.J., Kim, J.H., Joh, H.I., Kim, S.K., Moon, G.Y., Lim, T.H., Han, C., and Ha, H.Y. (2008). Sensor-less control of methanol concentration based on estimation of methanol consumption rates for direct methanol fuel cell systems. *International Journal of Hydrogen Energy*, 33(23), 7163–7171.
- Skogestad, S. (2003). Simple analytic rules for model reduction and PID controller tuning. *Journal of process control*, 13(4), 291–309.
- Zenith, F. (since 2008). The Fremen project. URL https://bitbucket.org/fzenith/fremen. 096629e.
- Zenith, F. and Krewer, U. (2010). Modelling, dynamics and control of a portable DMFC system. *Journal of Process Control*, 20(5), 630–643.
- Zenith, F. and Krewer, U. (2011). Simple and reliable model for estimation of methanol cross-over in direct methanol fuel cells and its application to methanolconcentration control. *Energy & Environmental Science*, 4(2), 519–527.