State space model of the direct methanol fuel cell

J.Ch. Schlake, Ch. Preusse*, J. Winkelhake, U. Konigorski

Institute of Electrical Information Technology, Clausthal Technical University, Leibnizstraße 28, 38678 Clausthal, Germany

Abstract

In this report we propose a state space model of a direct methanol fuel cell. This dynamical model allows analysis and optimisation of the fuel cell in a control-theoretical framework, for instance to improve the overall dynamics of the fuel cell or to reject environmental disturbances. The model is particularly well suited to synthesise controllers, which are necessary to ensure stable, robust and efficient operation of a fuel cell. To yield a state space model of the direct methanol fuel cell, a system of nonlinear partial differential equations is transformed into a system of ordinary initial value problems by Laplace transforms, approximation in function spaces and the method of weighted residuals.
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1. Introduction

As a result of the increasing usage of accumulators, exploring alternatives to conventional batteries is becoming more and more interesting. A promising possibility is the concept of fuel cells. Fuel cells are expected to reach higher degrees of efficiency because of the direct conversion of chemical energy into electrical energy. Furthermore, they produce little noise and do not need large down times caused by charging.

The direct methanol fuel cell (DMFC) is especially promising for mobile applications with strongly limited space and weight. Compared to other fuel cells, it has a simple system design which leads to little required space. Currently, some applications in laptops, sailing boats etc. have already been reported. Yet the existing DMFCs are not competitive with respect to cost/performance ratio. In order to optimise existing cells it is important to analyse and, if necessary, to control its dynamical behaviour, e.g. [1,8].

While general models of a DMFC have already been formulated, many of them solely describe the steady state behaviour. At the Institute of Chemical Process Engineering at Clausthal Technical University, Germany, a dynamical model for a DMFC has been set up. This model describes methanol, oxygen, carbon dioxide, temperature, ionic and electrical potential in the fuel cell and allows dynamical simulations with variable temperature for one- and two-dimensional problems [7] by means of partial differential equations (PDEs). Based on these PDEs, a finite element model (FEM) has been developed to analyse and optimise a particular DMFC operated at the same institute. As a result, it is possible to simulate the reaction of the fuel cell to certain changing conditions, particularly to the anodic concentration of methanol and to the overall voltage.

In order to optimise the DMFC it is necessary to improve its dynamics. Control theory is the approved framework to deal with the dynamics of self-acting, aimed manipulation of the inputs to achieve a desired output. Control theory also provides heaps of standard procedures to design a controller for a certain input/output behaviour. Nevertheless, it is necessary to transform the partial differential equations of the mathematical model into an equivalent standard form, the state space model, which is a system of first-order ordinary differential equations. One approach of this transformation which is mathematically appealing yet easy to perform is described in this article.

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* Corresponding author.
  E-mail address: preusse@iei.tu-clausthal.de (Ch. Preusse).
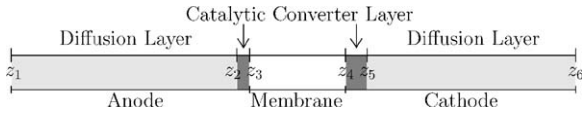*URL:* http://www.iei.tu-clausthal.de (Ch. Preusse).

Fig. 1. Subdivision of the MEA into five regions.

2. Dynamical model of the DMFC

In this article the dynamical behaviour of the DMFC is characterised by functions of place z and time t for methanol, oxygen, carbon dioxide and electrical and ionic potential. Temperature changes and water flow will be neglected, since they show but little influence on the dynamics of the DMFC (see [7]).

The model of the dynamical behaviour of the DMFC is restricted to its main part, the membrane electrode assembly (MEA). Generally, the MEA can be divided into five regions, namely two catalytic converter layers, where the oxidisation and the reduction takes place, two diffusion layers, which feed the catalytic converter layers with oxygen and methanol, and a membrane. They are shown in Fig. 1. The partition into five layers is caused by several physical parameters due to different materials. The modelling of a DMFC is restricted to one spatial dimension. The approach may well be extended to a two-dimensional model, yet the error of a one-dimensional model is less than 10% (see [3]).

Based on conservation laws, Rosenthal [7] obtained a set of PDEs for the quantities concentration of methanol c_{Me}, of oxygen c_{O_2} and of carbon dioxide c_{CO_2} as well as partial pressure of oxygen p_{O_2} and carbon dioxide p_{CO_2}. Additionally,

$$f_{Me} = \begin{cases} 0 & \Leftarrow z \in I_1 \\ k_2 \exp(k_3(\varphi_a - \varphi_m - k_4))c_{Me} & \Leftarrow z \in I_2 \\ \dfrac{\partial}{\partial z} c_{Me}\left(k_{19}\dfrac{\partial c_{O_2}}{\partial z} + k_{20}\dfrac{\partial c_{CO_2}}{\partial z} + k_{21}\dfrac{\partial \varphi_m}{\partial z}\right) & \Leftarrow z \in I_3 \\ k_5 \exp(k_3(\varphi_k - \varphi_m - k_4))c_{Me} & \Leftarrow z \in I_4 \\ 0 & \Leftarrow z \in I_5. \end{cases} \tag{2}$$

the model includes boundary value problems of the electrical potentials φ_a and φ_k as well as of the ionic potential φ_m. The spatial domains of the differential equations are the regions shown in Fig. 1. Their physical dimensions for the MEA belonging to the DMFC described in [7] are

$$I_1 = (z_1, z_2) = (0, 520 \ \mu m),$$

$$I_2 = (z_2, z_3) = (520, 550 \ \mu m),$$

$$I_3 = (z_3, z_4) = (550, 760 \ \mu m),$$

$$I_4 = (z_4, z_5) = (760, 810 \ \mu m),$$

$$I_5 = (z_5, z_6) = (810, 1330 \ \mu m).$$

The model of the MEA uses liquid and gas phases, both reacting independently, whereas the void ratio is supposed to be uniform at the whole MEA. To simplify matters, these equations are confined to reduction of oxygen and oxidation of methanol while neglecting intermediate reactions. Instead, the global kinetics of the ideal equation of reaction is used.

2.1. Differential equations

According to the diffusion law by Fick, the concentration of methanol c_{Me} is described in all regions by diffusion equations:

$$\frac{\partial c_{Me}(t, z)}{\partial t} = k_1 \frac{\partial^2 c_{Me}(t, z)}{\partial z^2} + f_{Me}(t, z) \tag{1}$$

for $t \in (0, T]$ and $T \in \mathbb{R}$. The constants k_i for any index i here and in all following equations are placeholders for physical parameters of the DMFC. They may vary between different layers. A complete account of equations and constants can be found in [7].

Inevitably, no known membrane inhibits methanol crossover completely. Hence, methanol passes through the membrane by diffusion, convection (the whole fall of pressure difference takes place in the membrane) and migration of the protons (molecules of methanol are dragged through the membrane), and thus may interchange between anodic and cathodic layers. These additional effects are reflected by three terms in $f_{c_{Me}}$ in the region I_3. The oxidation of methanol takes place in the catalytic converter layers I_2 and I_4. Hence, the right-hand side of Eq. (1) is given by

Inside the membrane oxygen and carbon dioxide are described by concentrations c_{O_2} and c_{CO_2}. The PDEs for $z \in I_3$ are similar to Eq. (1) with $f_{O_2} = f_{CO_2} = 0$. Outside the membrane both gases are described by partial pressures p_{O_2} and p_{CO_2}. Their dynamics is represented with $t \in (0, T]$ and $z \in I_1 \cup I_2 \cup I_4 \cup I_5$ by four nonlinear PDEs:

$$\frac{\partial p_{O_2, CO_2}(t, z)}{\partial t} = \frac{\partial}{\partial z} N\left(p_{O_2}, p_{CO_2}, \frac{\partial p_{O_2}}{\partial z}, \frac{\partial p_{CO_2}}{\partial z}\right) + f_{O_2, CO_2}(t, z). \tag{3}$$

The nonlinear transport term $N(p_{O_2}, p_{CO_2}, \partial p_{O_2}/\partial z, \partial p_{CO_2}/\partial z)$ in Eq. (3) describes the transport of oxygen and carbon dioxide outside the membrane by a Binary–Friction-model.

The nonlinear terms f_{O_2} and f_{CO_2} are given by

$$f_{O_2} = \begin{cases} 0 & z \in I_1 \\ k_{22} \exp(k_8(\varphi_a - \varphi_m - k_9))p_{O_2} & z \in I_2 \\ k_{23} \exp(k_8(\varphi_k - \varphi_m - k_9))p_{O_2} & z \in I_4 \\ 0 & z \in I_5 \end{cases} \quad (4)$$

and

$$f_{CO_2} = \begin{cases} 0 & z \in I_1 \\ k_{24} \exp(k_3(\varphi_a - \varphi_m - k_4))c_{Me} & z \in I_2 \\ k_{25} \exp(k_3(\varphi_k - \varphi_m - k_4))c_{Me} & z \in I_4 \\ 0 & z \in I_5, \end{cases} \quad (5)$$

which represent in I_2 and I_4 the reduction of oxygen and the synthesis of carbon dioxide by oxidation of methanol, respectively.

The electrical and ionic potentials φ can be described similarly to c_{Me}. Yet the dynamics of φ is much faster than the changes of c_{Me}. The dynamics of the potentials may therefore be neglected, so that their behaviour is described solely by boundary value problems. Thus, the potentials φ are described by time-independent PDEs:

$$0 = k_{16} \frac{\partial^2 \varphi_a(z)}{\partial z^2} + f_{\varphi_a}(z), \quad z \in I_1 \cup I_2, \quad (6)$$

$$0 = k_{17} \frac{\partial^2 \varphi_m(z)}{\partial z^2} + f_{\varphi_m}(z), \quad z \in I_2 \cup I_3 \cup I_4 \quad \text{and} \quad (7)$$

$$0 = k_{18} \frac{\partial^2 \varphi_k(z)}{\partial z^2} + f_{\varphi_k}(z), \quad z \in I_4 \cup I_5. \quad (8)$$

The nonlinear terms:

$$f_{\varphi_a} = \begin{cases} 0 & z \in I_1 \\ k_6 \exp(k_3(\varphi_a - \varphi_m - k_4))c_{Me} + k_7 \exp(k_8(\varphi_a - \varphi_m - k_9))p_{O_2} & z \in I_2, \end{cases} \quad (9)$$

$$f_{\varphi_m} = \begin{cases} k_{10} \exp(k_3(\varphi_a - \varphi_m - k_4))c_{Me} + k_{11} \exp(k_8(\varphi_a - \varphi_m - k_9))p_{O_2} \quad z \in I_2 \\ 0 \quad z \in I_3 \\ k_{12} \exp(k_3(\varphi_k - \varphi_m - k_4))c_{Me} + k_{13} \exp(k_8(\varphi_k - \varphi_m - k_9))p_{O_2} \quad z \in I_4, \end{cases} \quad (10)$$

$$f_{\varphi_k} = \begin{cases} k_{14} \exp(k_3(\varphi_k - \varphi_m - k_4))c_{Me} + k_{15} \exp(k_8(\varphi_k - \varphi_m - k_9))p_{O_2} & z \in I_4 \\ 0 & z \in I_5 \end{cases} \quad (11)$$

reflect the potentials which depend on c_{Me} and p_{O_2}.

All in all, the dynamic model of the DMFC is given by three time-dependent PDEs for each region $I_1, \ldots, I_5$, a single time-independent PDE for each of the regions I_1, I_3 and I_5 and two time-independent PDEs for each of the regions I_2 and I_4. Ten of the time-dependent PDEs are nonlinear. Unfortunately, each quantity has a nonlinear right-hand side f in at least one region.

2.2. Boundary and initial conditions

To characterise the dynamic behaviour of the DMFC completely, two initial conditions and two boundary conditions are necessary for every PDE depending on time t in each region. Additionally, every time-independent PDE needs two spatial boundary conditions for each region.

The initial values for the PDEs in Section 2.1 can be chosen arbitrarily. For instance, $p_{O_2}(0, z)$ and $p_{CO_2}(0, z)$ as initial values for Eq. (3) reflect merely partial pressures at $t = 0$. They are determined by certain environmental conditions.

The boundary conditions may be separated into two groups. The boundary values of the MEA at $z = z_1 = 0$ μm and $z = z_6 = 1330$ μm are determined again by some environmental conditions and may be chosen arbitrarily. In contrast, the inner conditions at the layer contacts at $z = z_2, \ldots, z_5$ have to reflect the physical properties of the MEA. In general, any solution of the PDEs must be continuous on the entire MEA. Hence, the inner boundary conditions are equalities between left-hand and right-hand sides. For p_{O_2} in Eq. (3) for instance, the inner boundary conditions read:

$$p_{O_2,l}(t, z_i) = p_{O_2,r}(t, z_i), \quad i = 2, \ldots, 5 \quad (12)$$

for $t \in (0, T]$. Here as well as in the entire sequel, the index l marks the left-hand value at z_i and r accordingliy the right-hand value at z_i:

$$p_{O_2,l}(t, z_i) = \lim_{\varepsilon \to 0} p_{O_2}(t, z_i - \varepsilon) \quad \text{and}$$

$$p_{O_2,r}(t, z_i) = \lim_{\varepsilon \to 0} p_{O_2}(t, z_i + \varepsilon), \quad i = 1, \ldots, 5.$$

Additionally, the right-hand sides of the PDEs of Section 2.1 describing the material flow must be at least continuous. Therefore, additional inner boundary conditions are given by, here exemplarily in case of Eq. (3):

$$N_l = N_r \quad \text{at} \quad z = z_2, \ldots, z_5.$$

Generally, with y being a placeholder for concentrations and partial pressures, the set of conditions can be summarised as

$$B_r y(t, z_i) = y_r(t) \quad \text{and} \quad B_l y(t, z_{i+1}) = y_l(t) \quad (13)$$

with operators B_l and B_r for each differential equation and $i = 1, \ldots, 5$. The time-independent PDEs describing the electrical and ionic potentials have inner boundary conditions similar to Eq. (13), except that they are time-independent, too.

3. State space representation of the DMFC

The dynamics of the DMFC is represented by 15 nonlinear and 7 linear partial differential equations of degree two. This model of the DMFC is not well suited in a control-theoretical sense, i.e. to analyse the cells dynamic behaviour and to synthesise a proper controller. Therefore, these differential equations will be transformed into an equivalent mathematical formulation, the state space representation. A state space model allows detailed analysis of the cells temporal and spatial behaviour, optimisation of physical parameters of the cell and is well suited for synthesis of a controller to, e.g. stabilise the cells voltage or reject environmental disturbances. Besides, there are powerful tools for simulation, analysis, synthesis and optimisation of the dynamic behaviour of a state space model.

The transformation of the differential equations developed in Sections 2.1 and 2.2 into a state space model, i.e. a set of linear ordinary first-order differential equations will be carried out in several steps. Laplace transforms are applied to eliminate partial time derivatives. The result is a set of ordinary differential equations either of place z or of both frequency s and place z. Afterwards, the dependency upon place z is eliminated by the method of weighted residuals, that is by approximating the spatial dependency as accurately as required. Finally, the nonlinearities of the differential equations are treated to yield a numerically convincing yet linear approximation of the dynamics of the DMFC, which is the state space model, i.e. a system of ordinary linear second-order initial value problems [5].

3.1. Laplace Transform

With the Laplace transform:

$$Y(s, z) = \mathcal{L} y(t, z) = \int_{t=0}^{\infty} y(t, z) e^{-st} dt, \tag{14}$$

linear partial differential equations may be transformed into a boundary value problem:

$$DY(s, z) = U_{I_i}(s, z), \quad z \in I_i = (z_i, z_{i+1}) \subset \mathbb{R},$$
$$i = 1, \ldots, 5, \tag{15}$$

with D being a linear operator, which depends on the complex frequency parameter s (see [4]). Capital letters denote the corresponding time-dependent lowercase letters in the frequency domain, a notation which is adopted in the entire sequel. Applying the Laplace transform (14) to, for instance, Eq. (1), the partial differential equation in $c_{Me}(t, z)$ can be written as an ordinary boundary value problem in $C_{Me}(s, z)$ and reads:

$$sC_{Me}(s, z) - k_1 \frac{\partial^2 C_{Me}(s, z)}{\partial z^2} = \mathcal{L} f_{Me}(t, z) + c_{Me}(0, z). \tag{16}$$

The right-hand side of Eq. (16) is the equivalent of U_{I_i} in Eq. (15). U_{I_i} contains all possibilities to exert influence within the region I_i, $i = 1, \ldots, 5$. A description similar to (15) can be stated for all time-dependent PDEs introduced in Section 2.1.

A precondition for applying the Laplace transform to a PDE is, that neither mixed partial derivative occurs. For most physical systems this precondition is satisfied. Here too, all PDEs introduced in Section 2.1 include either spatial or temporal partial derivatives, but not mixed ones.

3.2. Method of weighted residuals and collocation

One of several possibilities to transform partial differential equations or boundary value problems is the method of weighted residuals [4]. The fundamental idea of this method is the approximation of the exact solution y by a linear combination:

$$\hat{y}(t, z) = \sum_{j=1}^{N} \bar{y}_j(t) \phi_j(z) \quad \text{or} \quad \hat{Y}(s, z) = \sum_{j=1}^{N} \bar{Y}_j(s) \phi_j(z) \tag{17}$$

of $N \in \mathbb{N}$ basis functions $\phi_j(z)$. Thus, solving PDEs or boundary value problems in $y(t, z)$ and $Y(s, z)$ is replaced by calculation of the coefficients $\bar{y}_j(t)$ and $\bar{Y}_j(s)$, respectively. The basis functions $\phi_j(z)$ in Eq. (17) can be arbitrarily chosen, they merely need to be linearly independent.

For modelling the DMFC, Chebyshev polynomials have been used as basis functions $\phi_j(z)$. They are an orthogonal set of functions, which will play a major role later (see Section 3.3). Furthermore, approximations based on Chebyshev polynomials converge rather fast, hence only few basis functions are necessary and N remains small. Not at least, calculations based on simple polynomials are computationally cheap [6].

The main advantage of the method of weighted residuals is a small number of basis functions N compared to several other approaches. This leads to a comparatively small dimension of the resulting system of linear equations. Moreover, the solution is approximated not only at certain discretisation points. The coefficients $\bar{y}_j(t)$ represent $y(t, z)$ at every point in the region I_i, likewise for Laplace transformed quantities. Thus, interpolation is avoided when evaluating $y(t, z)$ or $Y(s, z)$ at some $z \in I_i$, $i = 1, \ldots, 5$, which is particularly important for system analysis.

The coefficients $\bar{y}_j(t)$ and $\bar{Y}_j(s)$ have to be calculated respecting two constraints. Namely, the approximating function $\hat{y}$ or $\hat{Y}$ resp. has to satisfy the boundary value problem (15) as well as the corresponding boundary conditions (13).

The coefficients $\bar{y}_j(t)$ of Eq. (15) are calculated by minimisation of the approximation errors $R_N = D\hat{y}(t, z) - Dy(t, z)$ and $R_N = D\hat{Y}(s, z) - DY(s, z)$ resp., i.e. the weighted residuals:

$$r_k = \int_{z_i}^{z_{i+1}} R_N w_k(z) dz, \quad k = 1, \ldots, N-2, \ i = 1, \ldots 5, \tag{18}$$

should vanish. With a set of $N-2$ weighting functions $w_k(z)$, (18) is a system of $N-2$ equations to determine the N coefficients $\bar{y}_j(t)$ or $\bar{Y}_j(s)$. Two equations are yet required to uniquely solve (18). They are given by the boundary conditions (see Eqs. (21) and (22) below).

The weighting functions $w_k(z)$ can be arbitrarily chosen, they only need to be linearly independent. The simplest choice is the Dirac impulse at some point $z_{\mathrm{cp},k}$, which is called collocation, pseudospectral or method of selected points, $w_k(z) = \delta(z, z_{\mathrm{cp},k})$ for $k = 1, \ldots, N-2$. Now the weighted residuals (18) reduce to $r_k = R_N(s, z_{\mathrm{cp},k})$ or $r_k = R_N(t, z_{\mathrm{cp},k})$ for $k = 1, \ldots, N-2$.

For boundary value problems without time-dependency follows:

$$\sum_{j=1}^{N} \bar{y}_j \underbrace{D\phi_j(z_{\mathrm{cp},k})}_{=v_{kj}} = \underbrace{u_{I_i}(z_{\mathrm{cp},k})}_{=\hat{u}_k}, \quad k = 1, \ldots, N-2. \quad (19)$$

For s-depending boundary value problems the method of weighted residuals for $k = 1, \ldots, N-2$ results in linear equation systems depending on s:

$$\sum_{j=1}^{N} \bar{Y}_j(s) \left(ks \underbrace{\phi_j(z_{\mathrm{cp},k})}_{=w_{kj}} + \underbrace{D_z\phi_j(z_{\mathrm{cp},k})}_{=v_{kj}} \right) = \underbrace{U_{I_i}(s, z_{\mathrm{cp},k})}_{=\hat{U}_k(s)}. \quad (20)$$

Here, the operator D is replaced by a place-depending, time-invariant operator D_z and a time-variant operator. Since all PDEs of the DMFC are of degree one for the derivation with respect to time, the time-variant operator can be written as ks and $k(\partial/\partial t)$, respectively.

With $\hat{y}$ or $\hat{Y}$ resp. satisfying the boundary value problem (15), they still have to fulfill the corresponding boundary conditions (13). According to Section 2.2, all inner and outer boundary conditions at $z = z_1, \ldots, z_6$ can be written in a standardised form with operators. They shall be transformed similarly to Eq. (19) in case of a boundary value problem and Eq. (20) for a partial differential equation.

Applying Eq. (17) to Eq. (13) yields:

$$B_r \sum_{j=1}^{N} \bar{y}_j\phi_j(z_i) = y_r \quad \text{and} \quad B_l \sum_{j=1}^{N} \bar{y}_j\phi_j(z_{i+1}) = y_l,$$
$$i = 1, \ldots, 5 \quad (21)$$

for time-independent boundary value problems and

$$B_r \sum_{j=1}^{N} \bar{Y}_j(s)\phi_j(z_i) = Y_r(s) \quad \text{and}$$
$$B_l \sum_{j=1}^{N} \bar{Y}_j(s)\phi_j(z_{i+1}) = Y_l(s), \quad i = 1, \ldots, 5, \quad (22)$$

for frequency-depending boundary value problems.

Eq. (19) resp. (20) together with Eq. (21) resp. (22) completely characterise the approximation $y(z)$ resp. $Y(s, z)$ according to Eq. (17) of the solution of the DMFCs model introduced in Section 2.1.

3.3. Linear state space model of the DMFC

For all seven time-independent boundary value problems we recall Eq. (19) and define the quantities:

$$\bar{y} = (\bar{y}_j) \in \mathbb{R}^{7N}, \qquad \hat{u} = (\hat{u}_i) \in \mathbb{R}^{7N} \quad \text{and}$$
$$V = (v_{kj}) \in \mathbb{R}^{7N \times 7N}.$$

On the other hand, for each of the three frequency-depending boundary value problems, we define according to Eq. (20):

$$\bar{Y}(s) = (\bar{Y}_j(s)) \in \mathbb{R}^{5N}, \qquad \hat{U}(s) = (\hat{U}_i(s)) \in \mathbb{R}^{5N} \quad \text{and}$$
$$V = (v_{kj}) \in \mathbb{R}^{5N \times 5N}, \qquad W = (w_{ij}) \in \mathbb{R}^{5N \times 5N}.$$

Now, time-independent boundary value problems (19) can simply be written as a linear matrix equation:

$$V\bar{y} = \hat{u}. \quad (23)$$

Similarly, frequency-depending boundary value problems (20) now simply read:

$$(ksW + V)\bar{Y}(s) = \hat{U}(s). \quad (24)$$

Eqs. (23) and (24) are a linear state space model of the DMFC. Yet, for efficient analysis, optimisation and synthesis of the dynamical system further transformations are necessary to yield a simple input/output relation.

The rows of V, Eq. (23), are created either by the method of weighted residuals (in total $7(N-2)$ rows) or by boundary conditions (7×2 rows). The latter ones are pairwise linearly independent, if only the boundary conditions at z_1 and z_6 are of Dirichlet type. This applies to the DMFC as can be seen in Eq. (21). The $7(N-2)$ rows of V created by the method of weighted residuals are pairwise linearly independent, if the set of basis functions $\phi_j(z)$, $j = 1, \ldots, N$ (see Eq. (17)), is orthogonal. Since both sets of rows are necessarily linearly independent, the matrix V is regular for orthogonal basis functions.

With a regular matrix V, Eq. (23) reads:

$$\bar{y} = V^{-1}\hat{u}$$

with $\bar{y}$ being the unique solution for the corresponding time-independent boundary value problems.

Frequency-depending boundary value problems cannot be transformed similarly, since the left-hand side of Eq. (24) depends on the frequency parameter s. Though, Eq. (24) may be further transformed to

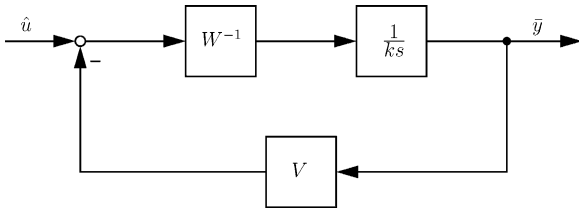$$s\bar{Y}(s) = \frac{1}{k}W^{-1}(-V\bar{Y}(s) + \hat{U}(s)) \quad (25)$$

Fig. 2. Block diagram of the state space model of linear partial differential equations.

if only W is regular. For general boundary conditions, and boundary conditions of the DMFCs model, too, the regularity of W cannot be guaranteed. Nevertheless, the boundary conditions of the DMFC may be transformed to a differential equation, if they are differentiated in time, and thus create a regular matrix W.

Reverse Laplace transform of Eq. (25) yields a linear state space model of time-dependent boundary value problems:

$$\dot{\bar{y}}(t) = \frac{1}{k}W^{-1}(-V\bar{y}(t) + \hat{u}(t)), \quad t \in (0, T]. \tag{26}$$

Altogether, the dynamical behaviour of the DMFC is captured by a state space model (26) with

system matrix : $\quad A = -\dfrac{1}{k}W^{-1}V \quad$ and

input matrix : $\quad B = \dfrac{1}{k}W^{-1}. \tag{27}$

Fig. 2 shows the corresponding block diagram for Eq. (26). The input vector $\hat{u}$ is given by $5(N-2)$ values $\hat{u}_i(t)$ included in $U(s, z)$ at collocation points $z_{cp,k}$ (see Eq. (15)). The remaining 5×2 values are the boundary conditions, i.e. the derivative of the right-hand sides of Eq. (13). The output vector $\bar{y}(t)$ consists of coefficients $\hat{y}_j(t)$, which in fact represent the solution of the partial differential equation.

3.4. Linear time-variant state space model of the DMFC

The results of Section 3.3 do not yet incorporate any nonlinearity of the partial differential equations introduced in Section 2.1. To yield a linear state space model for analysis, optimisation and control of the DMFC, all nonlinear terms must be eliminated. Of course, any kind of linearisation of the differential equations is straightforward. But a priori no guaranteed error bounds can be stated explicitly. To reduce the linearisation errors and particularly keep the solution in tight error bounds, linear approximations of the nonlinear terms are calculated iteratively.

Here again, the method of weighted residuals is proposed. Two possibilities are at hand. The first one is a classical Newton iteration, in which the nonlinear problem is discretised with the method of weighted residuals. The resulting nonlinear matrix equation can be solved iteratively by linearisation (see e.g. [9]). The second possibility is to linearise about a function and discretise the linear problem afterwards. The second variant is the Newton–Kantorovich method. It is pre-

ferred in this context [2], since it is computationally much cheaper and numerically more stable.

Yet there is another possibility to yield a state space model in a control-theoretical framework. Accepting a slight change in the notion of states, the nonlinearities in partial differential equations similar to Eq. (1) or (3) may be considered as time-depending variation of the states, i.e. as auxiliary inputs $u_a(t, z)$. Applying Laplace transform and collocation, they shall read $\hat{U}_a(s) = \mathcal{L}u_a(t, z_{cp,k})$ at collocation points $z_{cp,k}$, $k = 1, \ldots, N-2$. Of course, no external influence on the DMFC can be exerted with these auxiliary inputs. Instead, all additional inputs are already determined by the partial differential equations.

With these auxiliary inputs, Eq. (25) will be extended to

$$s\bar{Y}(s) = \frac{1}{k}W^{-1}(-V\bar{Y}(s) + \hat{U}(s) + \hat{U}_a(s)). \tag{28}$$

The matrices V, W and the input term $\hat{u}_a$ are the same as in (25). The inputs $\hat{U}_a(s)$ are completely determined by the PDEs. Consequently, their dependency upon time or frequency resp. can be rewritten as time-variant dependency upon the states of the state space model of the DMFC. As an example, the concentration of methanol c_{Me} (see Eq. (1)), shall be considered in the anodic catalytic converter layer I_2 (see Fig. 1 in Section 2). There, $\hat{u}_a(t)$ reduces to a term $V_a(t)\bar{y}$ depending on time t. The entries of $V_a(t)$ are given by

$$(V_a)_{k,j} = k_2 \exp(k_3(\varphi_a(z_{cp,k}) - \varphi_m(z_{cp,k}) - k_4))\phi_j(z_{cp,k})$$

for $k = 1, \ldots, N-2$ and $j = 1, \ldots, N$. The entries still missing, i. e. the remaining two rows of $V_a(t)$, are determined by the corresponding boundary conditions (see Section 3.3).

Similarly to Eq. (25), the reverse Laplace transform of Eq. (28) yields a linear state space model of the nonlinear boundary value problems:

$$\dot{\bar{y}}(t) = \frac{1}{k}W^{-1}(-V\bar{y}(t) + V_a(t)\bar{y}(t) + \hat{u}(t)), \quad t \in (0, T]. \tag{29}$$

The dynamical behaviour of the DMFC represented by a state space model (29) has an input matrix similar to Eq. (27). The system matrix is divided into a time-independent part $W^{-1}V$ and a time-depending part $W^{-1}V_a(t)$, i.e.

system matrix $\quad A = \dfrac{1}{k}(-W^{-1}V + W^{-1}V_a(t)) \quad$ and

input matrix $\quad B = \dfrac{1}{k}W^{-1}. \tag{30}$

The corresponding block diagram for Eq. (27) in conjunction with Eq. (28) can be seen in Fig. 3.

4. Results and discussion

The state space model of the entire DMFC is a composition of system and input matrices. Each partial differential
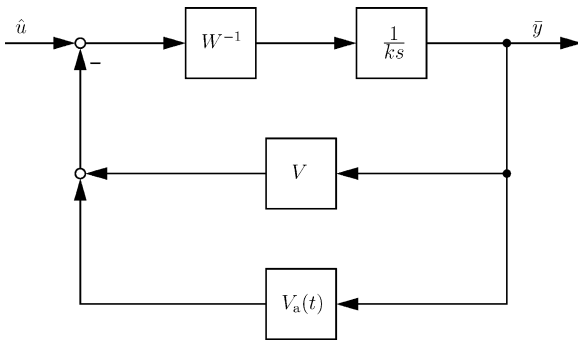
Fig. 3. Block diagram of the state space model of nonlinear partial differential equations.
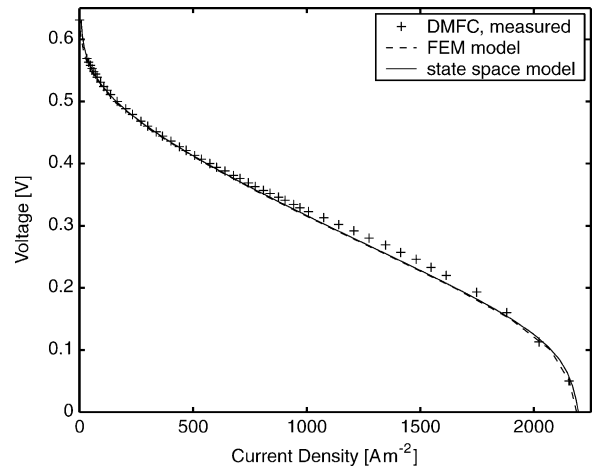

Fig. 4. current density–voltage characteristic; applied boundary conditions are $p_{CO_2}(z_1) = 1$ bar, $p_{CO_2}(z_6) = 0$ bar, $p_{O_2}(z_1) = 0$ bar, $p_{O_2}(z_6) = 1$ bar and $c_{Me}(z_1) = 750$ mol m^{-3}, $c_{Me}(z_6) = 0$ mol m^{-3}.

equation provides a state space model according to Eq. (26) or (29) resp. Consequently, the block diagram of the state space model of the DMFC is composed of several block diagrams shown in Figs. 2 and 3.

To validate the approach of modelling the DMFC in a control-theoretical framework, the state space model has been simulated for several environmental conditions, i.e. boundary and initial values. The results have been compared with simulation results of the FEM model of the PDEs developed by Rosenthal [7]. Additionally, measuring data of the DMFC described by Rosenthal have been taken into account if available.

An important and widely used quality of a fuel cell is its current density–voltage characteristic. It has been simulated and compared for various environmental conditions. Examplarily, a state space simulation, a FEM simulation and measuring data for a single set of boundary conditions, which are specified in the caption, are presented in Fig. 4. As can be seen, the state space model closely resembles the FEM model. Even though in the state space model the temperature is fixed, the differences between the FEM model and the state space model are negligible. The errors between the models and the original data are caused be the simplifications listed in Section 2.

The current density–voltage-characteristic plots the cells voltage against the steady state working point of the current density for constant boundary values and physical parameters. It allows the analysis of effects certain parameters show upon the performance of the DMFC when operated stationarily. Subsequently, environmental conditions as well as physical parameters can be altered to optimise particular properties of the cell.

Yet the state space model is particularly well suited for dynamical simulations. The step response is a standard method to analyse the systems dynamical behaviour. An example is shown in Fig. 5. The methanol concentration $c_{Me}(z_1)$ at the anodic outer boundary (solid step function) is stepwise altered at time $t = 0$ and 60 s. The plot shows the reaction of the state space model (solid line) and the reaction of the FEM model (dashed line) on this varying environmental condition. Here again, the state space model closely

resembles the FEM model. Which of both models reflects the cells dynamics more precisely cannot be evaluated, since no measuring data are available for pure steps of methanol concentration.

Yet the main advantage of the state space model cannot be shown in figures. Primarily, the state space model as a standard approach of control theory allows the analysis and optimisation of the cells dynamics. For instance, improving the behaviour of the cell in case of rapidly varying electrical load will be part of future work. The behaviour of the cell may also be improved by a closed loop controller, e.g. to stabilise the cells voltage by adaptation of methanol concentration. Again, a state space model is the preferred description a controller synthesis is based upon.

Another advantage of the state space model is the possibility of choosing the boundary values freely. The FEM model proposed by Rosenthal [7] is restricted to certain combinations of boundary values due to its inner structure. The
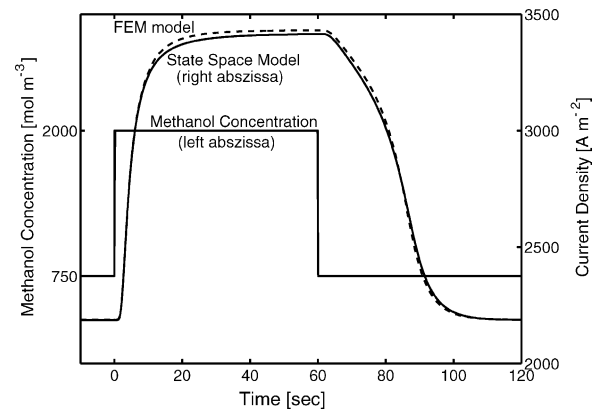

Fig. 5. Reaction of the cell to an anodic step of methanol concentration with boundary conditions $p_{CO_2}(t, z_1) = 1$ bar, $p_{CO_2}(t, z_6) = 0$ bar, $p_{O_2}(t, z_1) = 0$ bar, $p_{O_2}(t, z_6) = 1$ bar, $c_{Me}(t, z_6) = 0$ mol m^{-3} and $\varphi_k(t, z_6) = 0$ V.

inverse current density–voltage characteristic, for instance, can be calculated directly only by the state space model.

5. Conclusions

In this article, an approach is shown, which transforms the dynamical model of a direct methanol fuel cell into a state space representation. This representation is particularly well suited to analyse the systems dynamical behaviour, to optimise certain of its physical properties and to synthesise a controller when necessary. Therefore, the state space model is an important tool to develop robust and efficient applications of fuel cells. For instance, synthesis of a controller to ensure stable, robust and efficient operation of a direct methanol fuel cell will be part of future work.

Acknowledgements

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