Methodology for efficient parametrisation of electrochemical PEMFC model for virtual observers: Model based optimal design of experiments supported by parameter sensitivity analysis

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HIGHLIGHTS

- Analysis is based on a thermodynamically consistent electrochemical fuel cell model.
- Optimal set of fuel cell model parameters is determined by sensitivity analysis.
- D-optimal criterion is used to determine the optimal design of experiments.
- Enhanced parameter information results in up to few orders of magnitude lower RSE.
- It is shown that variation of inlet pressure significantly increases information.

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ABSTRACT

Determination of the optimal design of experiments that enables efficient parametrisation of fuel cell (FC) model with a minimum parametrisation data-set is one of the key prerequisites for minimizing costs and effort of the parametrisation procedure. To efficiently tackle this challenge, the paper present an innovative methodology based on the electrochemical FC model, parameter sensitivity analysis and application of D-optimal design plan. Relying on this consistent methodological basis the paper answers fundamental questions: a) on a minimum required data-set to optimally parametrise the FC model and b) on the impact of reduced space of operational points on identifiability of individual calibration parameters. Results reveal that application of D-optimal DoE enables enhancement of calibration parameters information resulting in up to order of magnitude lower relative standard errors on smaller data-sets. In addition, it was shown that increased information and thus identifiability, inherently leads to improved robustness of the FC electrochemical model.

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Proton exchange membrane fuel cells (PEMFC) are emerging as a feasible zero tank-to-wheel energy conversion technology for use in transport applications. Reduction and prevention of degradation effects of PEMFC and their influence on the remaining useful life, while retaining high performance of the PEMFC, are considered to be significant challenges towards their wider market adoption. Tackling these challenges under highly dynamic operations calls for precise on-line monitoring and control tools such as coupled virtual observers. 

Models used in observer applications should feature low computational effort, good extrapolation capabilities and should be easy to parametrise. As demand for low computational effort is obvious for on-line applications, good extrapolation capabilities significantly enhance applicability and accuracy of the observer model as they can be parametrised on small data sets, while still yielding high fidelity outputs in a larger operating region of a PEMFC. Therefore, application of data driven models, which are often used in the system level analyses, is hindered in studies aimed at combined performance and service life optimizations. This is mainly due to the fact that the accuracy of data driven models generally, does not reach beyond the trained variation space of parameters, which is in the area of a FC performance modelling alone a problem with multiple degrees of freedom (pressure, temperature, stoichiometry, concentrations, etc.).

This rationale motivates the use of the computationally fast reduced dimensionality electrochemical models e.g. Ref. [1-4], featuring a more profound mechanistic basis thus, exhibiting better prediction capability of the model. Development and validation of thermodynamically consistent reduced dimensionality electrochemical model for PEMFC [1] showed that identifiability and parametrisation of the model are crucial steps for successful utilization of system level models in predictive modelling and control applications. The need for increased identifiability of the parameters can be tackled with the reduction of the model or by using suitable experimental data in parametrisation procedure. Reduction of the model via reduction of calibration parameter set is meaningful, when parameters exhibit mathematical independence. In other cases, it should be avoided, since it hinders extrapolation capabilities of the model. On the other hand, obtaining experimental data is limited by time and cost constraints, therefore model based optimal design of experiments (DoE) shall be used to reduce necessary amount of experiments for successful parametrisation of the model.

Application of DoE enables reduction of full factorial DoE with an aim of minimizing the number of test runs required for successful parametrisation, while at the same time maximizing the accuracy of determined values of parameterised model. Its use in PEMFC ranges from applications focusing on designing individual components [5-8] and analysing their interrelations [9-11], over pinpointing the optimal operation conditions with an aim of lowering operational cost and increasing efficiency of the system [11-21] to determine the most suitable degradation mitigation strategy [22]. Furthermore, determination of optimal DoE for parameterisation purposes of the PEMFC model is utilized in works [23-26]. Majority of aforementioned studies use Taguchi method [7,9,12,13,17,18], fractional factorial DoE with response surface methodology [5,10,16,19-22,25,26] or a version of analysis of variance (ANOVA) [6,8,14,15,24,27], whereas in study by Rahim et al. [11] linear regression model is developed based on the results of full factorial DoE. In addition [28], provides an extended overview of the methodologies used for DoE and applications of DoE in PEMFC.

Application of model based DoE procedure is less common [23-27], however in case when model can be thermodynamically consistently derived from theory, it reduces the need for statistical modelling such as presented in Refs. [15], thus
Innovative contributions

Literature overview shows that model based DoE was performed only on simplified electrochemical models with reduced extrapolation capabilities with an aim of increased parameter identifiability. Consequently, this paper for the first time uses DoE approach on electrochemical model with state-of-the-art extrapolation capabilities [1] with an aim of answering three fundamental questions:

- “How to parametrise the reduced dimensionality electrochemical model of the FC in most optimal way with as little as possible experimental data?”
- “How many and which experiments shall be carried out to obtain necessary information about individual calibration parameters?”
- “How does a reduced space of operational points affect identifiability of individual calibration parameters of the model?”.

Methodology for answering this questions relies on innovative combination of newly developed model (presented in detail in Ref. [1]), which exhibits state-of-the-art extrapolation capabilities, and an approach for optimal selection of operational points for achieving ease of parametrisation. The latter, is based on application of D-optimal design plan applied on firstly experimental data set to determine most influential points for successful model calibration procedure and to determine smallest set of experimental data with which similar amount of information about individual calibration parameter is obtained. Secondly, the approach is also used on the synthetic space of experiments with an aim of determining theoretical optimal DoE for increasing identifiability of calibration parameters and thus, extremely increasing the model accuracy on one side and to significantly reduce experimental work load, which is needed for successful calibration of the model on the other. Innovative work flow therefore, can be used for both achieving reduced costs and efforts in parametrisation and reparametrisation procedures of modelling frameworks for virtual observers and for increasing model accuracy by increasing information about calibration parameters.

To consistently address presented problem and with that answer the posing fundamental questions, firstly Section Modelling framework briefly summarizes governing equations of the thermodynamically consistent electrochemical fuel cell model (TC FC model) that are relevant for parameter sensitivity analysis and model based optimization performed in this paper. In Section Methodology methodology for parameter sensitivity analysis and D-optimal DoE is then presented and division of synthetic space of experiments is laid out. Results of parameter sensitivity analysis and optimal selection of experimental points with highest information content from data set used in parametrisation procedure of the model are carried out in the Section Results and discussion. In addition, results of model based DoE applied on synthetic space of experiments are presented and show that equal or higher identifiability of calibration parameter on a smaller data set. Furthermore, effects of reduced synthetic space for variation of individual operational conditions are also studied in Section Results and discussion and in Section Conclusion the main conclusions are summarized.

Modelling framework

Thermodynamically consistent electrochemical model

Derivation of the 0D TC FC electrochemical model proposed in the scope of [1] relies on a mathematically consistent use of the sinus hyperbolicus definition on the Butler-Volmer (BV) equation. This approach results in an equation equivalent to the BV and that is defined over all current density ranges, thus establishing enhanced and easily invertible modelling basis in comparison to Tafel equation or linearized BV equation. The model is further extended to accommodate the transport of gaseous species along the channel and through the gas diffusion layer (GDL) yielding quasi-one-dimensional model. In the scope of this work it is used for model based DoE on experimental data and synthetic space of operational conditions with an aim of evaluating increased information of calibration parameters for each of the operational points. The main governing equation of the TC FC electrochemical model can be written as:
where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( e_0 \) is the elementary charge, \( \Delta g^0_0 \) and \( \Delta g^0_e \) are the differences in specific Gibbs free energy between reactants and products on the anode and cathode side and similarly \( \Delta s_0 \) and \( \Delta s_e \) are the specific entropy differences on the anode and cathode side, \( Z_a \) and \( Z_c \) are the number of electrons transferred in the electrochemical reaction on the anode and cathode side, values of \( \tilde{C}_{\text{H}_2}, \tilde{C}_0, \) and \( \tilde{C}_\text{H}_2 \) represent normalized values of concentrations of water, oxygen and hydrogen, respectively. Concentrations are normalized by the values obtained under standard ambient temperature and pressure conditions resulting in \( C_{\text{ref}} \) being 40.88 mol/m\(^3\). \( R \) is the resistance, \( I_0^a \) and \( I_0^c \) are intrinsic exchange current density on the anode and cathode side, respectively and can be for the latter defined as:

\[
\tilde{I}_0^c = ZFS \cdot e^{-\frac{C_{\text{H}_2}\left(T-T^0\right)\Delta s_0}{k_BT}} \cdot K_ce^{\frac{C_0\left(T-T^0\right)\Delta s_e}{k_BT}} \cdot I_0^c.
\]

and analogous for the anode side. Inserting the expressions for the newly determined calibration parameters \( \tilde{I}_0^a \) and \( \tilde{I}_0^c \) into Eq. (1) results in:

\[
U = \frac{k_B T}{eZ_c} \ln \left( \left( \tilde{C}_{\text{H}_2,0} \left( 1 + \frac{1}{I_{0\text{c}}} \right) \right)^2 \left( \tilde{C}_0 \left( 1 - \frac{1}{I_{0\text{c}}} \right) \right) \right) - \frac{k_B T}{eZ_a} \ln \left( \left( \tilde{C}_{\text{H}_2} \left( 1 - \frac{1}{I_{0\text{a}}} \right) \right)^2 \right) + \frac{\Delta g^0_0}{eZ_c} + \frac{(T-T^0)\Delta s_0}{eZ_c} + \frac{\Delta g^0_e}{eZ_a} + \frac{(T-T^0)\Delta s_e}{eZ_a} - RI

\]

where \( F \) is Faraday constant and \( S \) is active area of FC. For the anode side expression is analogous. On the other hand \( I_{0\text{a}}, I_{0\text{c}} \) are limiting currents which are defined as:

\[
I_{0\text{a},\text{c}} = ZFSD_{\text{a,c}} \cdot \frac{C_{\text{react}\text{a,c}}}{D_{\text{a,c}}} = ZFC_{\text{react}\text{a,c}} \cdot CD_{\text{a,c}},
\]

with \( C_{\text{react}\text{a,c}} \) being the concentration of reactants in the channel and \( D_{\text{a,c}} \) being the effective diffusivity through the GDL on the anode and cathode side. To determine a set of calibration parameters, firstly inputs based on the operational conditions and known physical constants such as (Faraday constant, elementary charge, specific Gibbs free energy differences, specific entropy differences etc.), were inserted into the model. The remaining parameters presented the set of calibration parameters: \( E_0, E_c, K_c, K_a, R, CD_a, CD_c \).

Reduction of calibration parameter set for near isothermal operation

In general reduction of the set of calibration parameters proves to be meaningful in case that they exhibit functional dependencies, and should be in other cases omitted, since it hinders extrapolation capabilities of the model. Analysis of the calibration parameters showed that \( E_0 \) and \( K_c \) for the cathode side and \( E_0 \) and \( K_a \) for the anode side in the Eq. (1) exhibit intertwined functional dependencies in case of near isothermal operation, which inherently means, that their unique determination is difficult or not possible, due to problem of solution space being infinite for a pair of functional dependant parameters [1]. The proposed reduction can be written as:

\[
\tilde{I}_0^c = ZFS \cdot e^{-\frac{\Delta g^0_0}{k_BT} - \frac{\Delta s_0}{k_BT}} \cdot K_c \cdot e^{\frac{\Delta g^0_e}{k_BT} - \frac{\Delta s_e}{k_BT}} \cdot I_0^c
\]

Table 1 – Operating conditions of FC under which polarisation curves were obtained.

<table>
<thead>
<tr>
<th>No.</th>
<th>( \lambda_{\text{an}} )</th>
<th>( \lambda_{\text{cat}} )</th>
<th>( p_{\text{max}} ) [bar]</th>
<th>( p_{\text{mean}} ) [bar]</th>
<th>RH_{\text{an}} [%]</th>
<th>RH_{\text{cat}} [%]</th>
<th>T [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,3</td>
<td>1,8</td>
<td>1,013</td>
<td>1,013</td>
<td>0</td>
<td>80</td>
<td>343,15</td>
</tr>
<tr>
<td>2</td>
<td>1,3</td>
<td>1,7</td>
<td>1,4</td>
<td>1,4</td>
<td>0</td>
<td>80</td>
<td>346,15</td>
</tr>
<tr>
<td>3</td>
<td>1,3</td>
<td>1,7</td>
<td>2,0</td>
<td>2,0</td>
<td>0</td>
<td>80</td>
<td>347,15</td>
</tr>
<tr>
<td>4</td>
<td>1,3</td>
<td>1,7</td>
<td>2,5</td>
<td>2,5</td>
<td>0</td>
<td>80</td>
<td>349,15</td>
</tr>
</tbody>
</table>

Methodology

The model presented in previous section will firstly be parametrised on the experimental data as presented in Subsection Experimental data and calibration of the model to prepare the basis for subsequent analyses. These analyses will be methodologically based on parameter sensitivity analysis.
presented in the Subsection Parameter sensitivity analysis, application of D-optimal DoE, presented in Subsection Optimal design of experiments, on experimental data set presented in Subsection Experimental data and calibration of the model and on generated synthetic space of experiments based on the methodology presented in Subsection Synthetic space of experiments.

Experimental data and calibration of the model

Experimental data used in the scope of this work consisted of 4 individual polarisation curves which were obtained at different operating conditions as defined in Table 1 on the FC stack.

Calibration of the model was performed in a way that model output was fitted to experimental data in terms of minimizing penalty function value. Furthermore, physically plausible constraints were introduced on the calibration parameters, which assured that for example negative values of calibration parameters could not be obtained. The calibration procedure was run with differential evolution algorithm, which is an evolutionary algorithm that does not need the optimization to be differentiable, which inherently means that it is less prone to get stuck in local minima and therefore, appropriate for global optimization problem.

The results of the calibrated TC FC electrochemical model show very good agreement between the model and experiment for single and multiple experiments calibrated at once, which can be seen from Fig. 1, where polarisation curves were normalized to the maximum current value obtained by stack at voltage of 0.58 V.

Parameter sensitivity analysis

To successfully reduce calibration times of the electrochemical model and to assure a high quality of fit, both of which are crucial for enhanced accuracy, extrapolation capabilities and robustness of the model, this section presents methodology for parameter sensitivity analysis that aims to determine identifiability of the model calibration parameters. Therefore, to analyse ease of parametrisation, which has a positive impact on reduced time and experimental data needed for successful parametrisation, aforementioned parameter sensitivity analysis is carried out. The latter was performed via analysis of the calibration parameter values obtained in a Monte Carlo like simulation procedure that included a genetic algorithm. To test this aspect of the model, a genetic optimization algorithm (Matlab - ga [30]) was run for single and multiple polarisation curves 500 times with 1000 generations each with a population size of 200 and Initial Population Range determined as 0.2θ. The initial vector θ consists of an already optimized set of parameters obtained from a calibration procedure with differential evolution on the FC electrochemical model. In this kind of analysis, each individual parameter has a certain amount of spread based on which probability density function can be obtained (Matlab - pdf [30]). The skewness and spread of the calculated probability density functions give and unique insight into parameter identifiability. Higher spreads of the probability density distribution hint towards parameters that are harder to be uniquely determined. On the contrary, calibration parameters, whose values can be easily determined show significantly smaller spread with a high peak in probability density function in the vicinity of the calibration parameter actual value. Described process of assessing the parameter sensitivity analysis of individual calibration parameter was performed for both versions of the model separately.

Optimal design of experiments

Successful determination of the set of calibration parameters presented in the previous section enables application of parametrised version of the electrochemical model, which can be then formally written as the following static equation:

\[ y = f(\theta, u). \]  

(6)

where the model output is defined as \( y = U \), the parameter vector for the reduced model as:

\[ \theta = [I_e, I_o, R, CD_e, CD_a]^T. \]  

(7)

and the inputs to the model as:

\[ u = [C_{O_2}, C_{H_2}, C_{H_2O}, T]^T. \]  

(8)
The relation from the operating conditions to the concentrations in the input vector above are obtained via basic thermodynamic calculations.

Note, that when fitting (6) to measured experimental data $\hat{y} = y + \epsilon_y$, where the measurement errors $\epsilon_y \sim \mathcal{N}(0, \sigma_y)$ are assumed to be Gaussian, the obtained estimate of the parameter vector is a stochastic variable as well. Assuming that the used estimator is consistent and $\hat{\theta} \in \mathcal{N}(\theta, \Sigma_\theta)$, the expected value of the parameter estimate will be equal to the “true” parameters:

$$E(\hat{\theta}) = \theta. \quad (9)$$

However, in practice $E(\hat{\theta})$ cannot be evaluated, and a numerical approximation would require vast amount of data and experiments which is seldom possible or economically reasonable to do. In order to evaluate the confidence of the estimated parameters, obtained from a finite data-set, it is necessary to determine the associated parameter co-variance $\Sigma_\theta$. A direct approximation would again require extensive experimental data and is therefore not suitable, however, there exists a lower bound on the parameter covariance defined by the Cramér-Rao inequality \[31\]:

$$\text{Cov}(\hat{\theta}) \geq F^{-1}. \quad (10)$$

Thereby, the matrix $F$ is the so-called Fisher information matrix which, for the present static model, is determined as:

$$F = \frac{1}{\sigma_y^2} \sum_{k=1}^{N} F_k = \frac{1}{\sigma_y^2} \sum_{k=1}^{N} \phi_k^T \phi_k, \quad (11)$$

with the parametric output sensitivity:

$$\phi_k = \frac{\partial y_k}{\partial \theta} = \left[ \frac{\partial f(\theta, u_k)}{\partial \theta_1} \cdots \frac{\partial f(\theta, u_k)}{\partial \theta_n} \right]. \quad (12)$$

The scalar $N$ denotes the number of experimental data points $(u_k, y_k)$, $k \in \{1, \ldots, N\}$. Note, that the Fisher information is depending on the input operating conditions $F(U)$, with the vector of stacked inputs $U = [u_1 \ldots u_n]^T$.

For the optimal design of experiments, it is desired to maximize the Fisher information matrix $F$, as this would reduce the covariance of the estimated parameters and subsequently increases their confidence and identifiability. The available degree of freedom for doing so is the vector of stacked inputs $U$ which in turn defines our experimental conditions. In order to quantify the maximization of the Fisher information matrix, a scalar criterion thereof is needed. One commonly found optimality criterion is:

$$J(u) = \det F(U). \quad (13)$$

An experiment that maximizes (13) is referred to as D-optimal \[32\].

Note, that since the electrochemical model is static, the individual terms $F_k$ in Eqn. (11) can be calculated separately and do not influence each other. It is therefore possible to determine the information content of each individual experimental point. On the one hand, this enables us to determine those data-points from a given experimental data set with the highest information, or on the other hand, to look for those experimental inputs $u_k$ that lead to a maximum in information for a given maximum number $N$ of data points. The latter approach is iteratively carried in a greedy search fashion by defining a multidimensional experimental grid for the available inputs. Afterwards, the information content of all possible input combinations is evaluated and the one with the highest D-optimal value is selected as the first experimental point $k = 1$. For the second experimental point, all remaining input combinations are evaluated and its contributions $F_k$ are added to the Fisher information of the first experimental point $F_1$. After evaluating the D-optimality of all possible combinations, the second experimental point is chosen as the one that led to a maximum of information according to objective function (13). This search procedure is carried out until a fixed amount of experimental points $N_{\text{max}}$ has been reached.

**Synthetic space of experiments**

Data set used for parametrisation of the model consists of four polarisation curves as presented in Subsection Experimental data and calibration of the model. Even though several operational conditions have been varied to obtain this four polarisation curves, this represent only a small fraction of space obtained by full factorial of operational conditions, which is in this work denoted as synthetic space of experiments. With an aim of D-optimal DoE analysis performed on all full factorial of operational conditions defined by test stand limitations synthetic space of experiments was strained onto interval of fixed step variations of individual operational conditions, namely:

- stoichiometric ratio on the anode side: [1.1, 2.1] with step size of 0.2
- stoichiometric ratio on the cathode side: [1.1, 2.1] with step size of 0.2
- temperature of the FC: [333.15 K, 358.15 K] with step size of 5 K
- pressure on the anode inlet: [1.1 bar, 2.7 bar] with step size of 0.2 bar
- pressure difference on the inlet of the anode and cathode: [−0.1 bar, 0.1 bar] with step size of 0.05 bar.

Resulting in experimental space with 9720 (6x6x6x9x5) different operating conditions of the FC, that is with the exclusion of changing electrical current drawn from FC stack. Each of these operating conditions served as an input into already parametrised TC FC electrochemical model. As a result 9720 synthetic polarisation curves were obtained. Individual points on polarisation curves were then analysed from the stand point attainment of maximum information according to objective function (13).

**Results and discussions**

**Parameter sensitivity analysis**

In this section, the parameter sensitivity analysis has been carried out with the aim of determining set of calibration
parameters that have highest identifiability, on the given data set consisting of 256 points on four polarisation curves and thus, improving modelling basis. This step presents one of the key steps in a direction of achieving higher robustness of the model on one hand and reducing computational burden of parametrisation and reparametrisation procedure on the other. To successfully tackle this problem parameter sensitivity was firstly applied on the model with full set of calibration parameters presented in Eq. (1). Results of the analysis are presented in Fig. 2a, which shows that calibration parameters $E_0^c$, $K_c$, $K_a$, $R$, $CD_c$ and $CD_a$ can be uniquely determined with high probability.

However, activation energy on the anode side ($E_0^a$) is showing high covariance with absence of a visible peak, and has thereby, low possibility to be uniquely determined on the given data set.

This identifiability issue can be addressed in two different ways. One being the operation of FC under distinctly different operating conditions where anode kinetics has a higher impact on the FC performance, as for example under fuel starvation or near fuel starvation regime, which are highly detrimental for state of health (SoH) of FC. On the other hand, the second option for increasing the identifiability of the entire set of applied calibration parameters is via reduction of the set of calibration parameters as presented in Subsection Reduction of calibration parameter set for near isothermal operation. This is ratiocinated by the fact that calibration parameters which cannot be uniquely determined cause decreased indentifiability of calibration parameters that can be otherwise uniquely determined. The latter proves to be more beneficial in normal operating conditions, as encountered in the analysed case, since increased identifiability of the calibration parameters depicting the anode kinetics results also in increased identifiability of all other calibration parameters as well. This phenomena, can be seen in Fig. 2b, where up to five times higher peaks and significantly reduced covariance of probability density functions can be observed, thus confirming that model parametrisation can be carried out successfully and uniquely. Due to the smaller set of calibration parameters the reduced model is also easier to parametrise and less computationally demanding during this procedure, which inherently translates to reduced parametrisation effort.

**Optimal design of experiments**

**Determination of smallest meaningful experimental data set**

Parameter sensitivity analysis has shown that for the reduced version of calibration parameters all of them can be sufficiently well determined on the proposed 256 experimental points data set. However, not all of those operational points have equal information content about the calibration parameters. To determine how many of the points are actually needed to obtain similar amount of information in comparison to the full data set and to answer the first fundamental question presented in Section Introduction, this section presents application of D-optimal DoE on the experimental data set at hand.

![Fig. 2](image1.png)

\[ \text{Fig. 2} \quad \text{Probability distribution of the normalized value of calibration parameters of TC FC electrochemical model on the interval } [0.5, 1.5] \text{ for a) original set of 7 calibration parameters and b) reduced set of 5 calibration parameters.} \]

![Fig. 3](image2.png)

\[ \text{Fig. 3} \quad \text{Evolution of values of diagonal elements of FIM over the span of entire experimental data set (256 experimental points on four polarisation curves).} \]
Results of this application are presented in Fig. 3, where evolution of values of diagonal elements of FIM with each added experimental point are shown. Significant changes in information about calibration parameter can be seen for first several experimental points, however after those increase in information is more gradual. Therefore, detailed analysis was performed using only 20 experimental points containing the most information about calibration parameters based on D-optimal criterion. Location of these points in U–I 2D space is presented in Fig. 4a. This experimental data set was selected intentionally due to its demanding structure for parametrisation procedure, since only one of the polarisation curves contains also region covering activation losses. Nonetheless, it is surprising to observe in Fig. 4a how well the curves contains also region covering activation losses. None-
Looking at the results, it can be seen that diagonal values of FIM are for the 20 most influential operational points in synthetic experimental space in general much higher than in the ones obtained with the experimental data set. This can be attributed to the fact that selection of operational points in the case of the synthetic experimental space can be performed from the full factorial of operational conditions, whereas in the case of experimental data set at hand only four polariisation curves were obtained. With this approach $CD_a$ is increased 4581 times, $CD_c$,12,658 times, $I_c$ is increased for 2.0%, $I_a$ is increased 2.2 times and $R$ is increased by 75%, resulting in up to 112.5 times lower relative standard errors of calibration parameter assessment. The results thus confirm the adequacy of the proposed approach for increased information about calibration parameters on the smaller data set, or the other way around, achieving similar or higher information of the calibration parameters on a much smaller data set. Furthermore, as a result of decreased time and experimental points needed for parametrisation and reparametrisation, cost of the procedure is reduced and procedure can be in some cases already done on the fly during the operation of the system.

D-optimal DoE performed on synthetic space of experiments shows that with only 20 experimental points a lot of information about individual calibration parameters can be obtained. In addition, in the case of $CD_a$ information is already much higher than it is in the case of the full experimental data set used for parametrisation of the electrochemical model. Both of which can be attributed, as already mentioned, to the fact that in the case of synthetic experimental space a full factorial of operational conditions can be chosen from. This difference is even more obvious when the synthetic space of the same size as the one used for parametrisation of the model is used, results of which are presented in Fig. 6a and b. Information about individual parameters is in that case up to 43,000 times higher when experimental points selected with D-optimal DoE from synthetic space of experiments are used for parametrisation. Thus with reasonable sized space information about calibration parameters is so much enhanced that it really offers extremely precise determination of their value and as a direct consequence results in much more accurate model.

Results presented in Fig. 6a shed a light also on the interpolation capabilities of the electrochemical model used in the scope of this work. Even though the size of data set used in significantly larger, there are only two points in the middle of the synthetic experimental space, which hints towards state-of-the-art interpolation capabilities of the model.

Fig. 5 – a) First 20 synthetic experimental points containing the most information about calibration parameters based on D-optimal criterion and b) Diagonal elements of FIM for this 20 synthetic experimental points.

Fig. 6 – a) Positioning of first 256 synthetic experimental points containing the most information about calibration parameters based on D-optimal criterion and b) Diagonal elements of FIM for these 256 synthetic experimental points.
Effects of reduced synthetic space dimensionality on identifiability of calibration parameters

In the real world applications, it often happens that not all of the variations of operational conditions are achievable, whether because of the design of the balance of plants components (BoP), current SoH of the system or because FC design prohibits it. Therefore, this subsection presents the analysis on the impact of an individual operational condition and thus, reducing synthetic space dimensionality, on identifiability of each of the individual calibration parameters. By assessing this effect the answer to the last of the three fundamental questions asked in the Section Introduction can be provided.

Analyses of identifiability of the calibration parameters were performed on 6 reduced dimensionality synthetic spaces, where for each of the spaces one operational condition has been fixed, namely:

- stoichiometric ratio on the anode side ($\lambda_{an}$)
- stoichiometric ratio on the cathode side ($\lambda_{cat}$)
- inlet pressure on the cathode and anode side together ($p + \Delta p$)

Fig. 7 – Change of diagonal values of FIM with respect to increasing synthetic space of experiments for a) intrinsic exchange current density on the cathode side - $I_{c0}$, b) intrinsic exchange current density on the anode side - $I_{a0}$, c) ohmic resistance - $R$, d) combined diffusivity parameter on the cathode side - $CD_{c}$, e) combined diffusivity parameter on the anode side - $CD_{a}$.
• temperature of the FC (T)
• pressure on the anode inlet (p)
• pressure difference on the inlet of the anode and cathode (Δp).

The results are presented in Fig. 7, where identifiability of calibration parameters obtained on the 20 experimental points selected by D-optimally from the individual reduced dimensionality synthetic spaces are benchmarked full synthetic space. It is evident that reduced dimensionality of the synthetic space of experiments affects the identifiability of all individual calibration parameter parameters. Physical reasoning for this outcome is different for each of the parameter and will be presented in the following sections. Due to similar dependencies calibration parameters describing anode and cathode side (intrinsic exchange current density and combined diffusivity) are analysed together.

Intrinsic exchange current densities. Covariance of probability distribution of the normalized value of intrinsic exchange current densities showed in Fig. 2b are relatively high. This hints towards lower possibility of unique determination, which is confirmed by the low diagonal values of FIM presented in Fig. 7a) and b). Careful analysis of these figures shows that the most influential operational condition for determination of these values is temperature, whereas there is little to no difference for all of the other operational conditions. Obtained result is physiochemical consistent, since temperature highly affects the chemical kinetics via change of equilibrium potential and reaction rate constants. Based on this rationale it can be concluded that operating temperature should always be varied for successful determination of both anodic and cathodic intrinsic exchange current densities.

Combined diffusivity. Reducing information about one of intertwined phenomena highly influences the determination of the other. In the case of model at hand combined diffusivity calibration parameters are the ones affected by all of the operational conditions varied. Fixing any one of them has an observable effect on the amount of information available about combined diffusivity parameters and can be explained by strictly physical rationale:

- **Temperature** of the FC effects the transport phenomena via changing water partial pressures and thus gaseous/liquid equilibrium. Consequently, molar ratios of all gaseous species are changed which affects also the effective diffusivities.
- **Pressure and pressure difference** influences transport phenomena in channels in GDL. Due to changed concentration profile along the channel and affects the effective diffusivities and chemical kinetics.
- **Stoichiometry** similarly to the pressure affects concentration fields along the channels and changes the ratio between convective and diffusive fluxes in the channel and have also an affect on liquid water mitigation and the overall transport phenomena in GDL.

Based on the provided rationale it is expected that identifiability of combined diffusivity calibration parameter is the best when full space of operational points is available and that temperature has the smallest impact on the determination of the combined diffusivity parameter. This is attributed to the fact that its effect is actually consequence of the effect that it has on all of the other operational conditions and not direct as it is the case with others. Nonetheless, it is still interesting yet intuitive, that fixing just the temperature of FC operation reduces identifiability in the first 20 operational points for almost two orders of magnitude for the cathode side (Fig. 7 d) - green line) and for approximately for 40% for the anode side (Fig. 7 e) - green line). Detailed analysis of the aforementioned figures shows that the most detrimental for identifiability of combined diffusivity parameters is fixing the pressure and pressure difference between the anode and cathode side, which is expected, since it follows directly from the definition of limiting current provided in Eq. (3). Lastly, it should be pointed out that probability distribution also plays a role in identifiability of individual parameter. That can be easily seen from the case of combined diffusivity on the cathode side, which is the lowest of all remaining five calibration parameters (Fig. 2b), thus a lot of data is needed for it to be determined uniquely.

**Ohmic resistance.** Parameter sensitivity analysis presented in section **Parameter sensitivity analysis** showed that ohmic resistance has low covariance of probability distribution due to linear functional dependence on the voltage output, thus hinting towards easier unique determination, which was confirmed in Figs. 3, 5a and 6b. In Fig. 7 c) it can be seen that the diagonal FIM values are even increased when reduced dimensionality synthetic space is used for the fixed pressure and fixed pressure and pressure difference between anode and cathode. Reasoning for this at the first glance interesting yet intuitive effect lies in the fact that the optimal selection of first 20 operating points is defined by the means of D-optimal selection. This means that the maximum value of FIM determinant is sought, resulting in the fact that highest changes in values of other calibration parameters effect also the one that is being observed. Described mathematical effect leads to increased identifiability of ohmic resistance when reduced identifiability of the combined diffusivities are observed to accommodate the change in determinant value.

**Conclusions**

This paper presents a novel methodology for optimal design of experiments that enables efficient parametrisation of thermodynamically consistent electrochemical proton exchange membrane fuel cell model for virtual observers. With application of D-optimal design of experiments three fundamental questions that are crucial for efficient application of the model
are answered. Innovative and application relevant contributions of this innovative methodology can be summarized as:

1. Methodology for optimizing set of calibration parameters enables determining the minimum set of uniquely defined parameters, which enables minimizing the size of required parametrisation data-set and thus calibration workload.

2. Comparison of information obtained with full experimental data set and D-optimal selection of only 20 experimental points of the full data set comprising 256 points, revealed that successful parametrisation can be carried out on a significantly smaller data set with a minor reduction in information about the individual calibration parameters.

3. Application of D-optimal DoE on full factorial of operational conditions enables further enhancement of calibration parameters information (CDa - 4581 times, CDc - 12,658 times, iₙ by 2.0%, iₙ - 2.2 times and R by 75%) on a smaller data-set resulting in up to few orders of magnitude lower relative standard errors. Additionally, increased information and thus identifiability, inherently leads to improved robustness of the FC electrochemical model.

4. Methodological analysis of effects of reduced space of operational conditions showed significant diminution in information (for up to 5 orders of magnitude) when operational pressure on the anode and cathode side are kept constant.

Due to these features, the proposed methodology for determining an optimal set of calibration parameters and D-optimal design plan can be characterized as a beyond state-of-the-art methodology in the area of virtual observer for fuel cells. This is confirmed by significant reduction of the size of required parametrisation data-set. The latter is on one hand reflected in the reduced computational time needed for the optimization, whereas much larger impact in terms of cost and effort reduction is realized on the fuel test bed due to a severe reduction of measurements. In addition, as proposed methodology is computationally very efficient, it can be applied in a fully coupled manner with the fuel cell test bed for direct guidance of computational very efficient, it can be applied in a fully coupled manner with the fuel cell test bed for direct guidance of computation. Additionally, increased information and thus identifiability, inherently leads to improved robustness of the FC electrochemical model.

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