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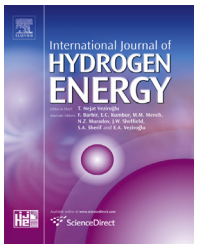

The application of design of experiments and response surface methodology to the characterization of a direct methanol fuel cell stack

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ARTICLE INFO

Article history:
Received 25 June 2015
Received in revised form
26 November 2015
Accepted 28 May 2016
Available online 16 June 2016

Keywords:
Direct methanol fuel cell
Stack modeling
Design of experiments
Regression models
Response surface methodology

ABSTRACT

This paper presents the results of a detailed characterization of a five-cell DMFC stack, obtained using a cubic experimental plan that was derived from design of experiments (DOE) methods. The results show that the operational behavior of a DMFC stack is mainly influenced by three independent input variables. Therefore four dimensional regression models were plotted against the input variables of temperature, electrical current density and the anode circuit's methanol concentration. The terms of these models were generated for the technically relevant operating range by applying a response surface methodology (RSM).

The generated models constitute a suitable starting point for follow-up modeling work of complete DMFC systems. The detailed characterization of a DMFC stack with mathematical models as an output is not available in the literature, so a data base for DMFC modeling can be provided to the scientific community. Additionally an application-oriented method for the characterization of DMFC stacks is described, which is an important tool for simulation-based development of DMFC stacks and systems.

Introduction

Fuel cells are electrochemical energy converters that transform a continuous feed of chemically bound energy into electrical energy. In many designs, hydrogen is used as the chemical energy carrier. However, for applications requiring electrical power below 5 kW, methanol offers certain advantages over hydrogen [1,2]. Methanol can, for instance, be directly utilized as fuel in direct methanol fuel cells (DMFCs). Methanol is easier to handle than hydrogen because of its liquid state and has an energy density some four times higher.

At the Forschungszentrum Jülich, a 1.3 kW DMFC system with a peak power of 7 kW was developed [3] over the last few years. The development and optimization of DMFC systems require extensive knowledge of the operating characteristics of DMFC stacks. On the one hand, it is necessary to optimize control processes to realize higher efficiencies and short startup times in the system. On the other, it is necessary to optimize the operation conditions of a DMFC stack on the basis of a deep understanding of its operational characteristics. Key challenges associated with DMFC technology include increasing efficiency by reducing methanol crossover through the membranes, which has a direct, negative effect on cell efficiency due to the loss of fuel. Water permeation through

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http://dx.doi.org/10.1016/j.ijhydene.2016.05.248

the membranes is also undesirable because in self-sufficient DMFC systems, recapturing water required for the anodic reaction is difficult [1]. Possible approaches to reduce methanol crossover and water permeation are to optimize the configuration of the electrodes and membranes used in cells or to develop operating strategies for DMFC stacks.

To improve the operational behavior of fuel cells within their developmental stages and operate them efficiently, it is important to comprehensively describe the operational behavior of DMFCs in the dependency of all relevant operating parameters. The operational behavior of a DMFC stack depends on the stack design and the MEAs used. Due to this reason it is desirable to generate a set of equations representing the operational characteristics of a certain stack configuration. Many past publications have focused on describing the operational behavior of single cells, some examples of which are given below.

Gurau et al. [4] measured methanol conversion in relation to the fuel flow rate, the temperature and methanol concentration. The data was visually depicted with three-dimensional surfaces. Nakagawa et al. [5] show the results of characterized cells and describe the correlation between cell voltage and the operational parameters of temperature, air-flow and current density by comparing various sets of curves. Santarelli et al. [6] explore the effects of the operating variables on the performance of a hydrogen fuel cell by varying six operational variables and comparing various sets of performance curves. Ge and Liu [7] study the effects of operating temperature, methanol concentration, anode flow rate, air-flow rate and cathode humidification on the voltage of a DMFC. The mentioned publications provide an overview about the most relevant operational variables but the results can hardly be transferred into mathematical terms for modeling purposes.

In order to correlate target values and factors in a comprehensive way, it is desirable to generate mathematical models describing their operational behavior. To generate mathematical models, it is possible to describe the microscopic processes with fundamental equations. The generation of these types of models is possible to the extent that occurring effects are known with precision. In the literature, publications of these so-called "white box" models for fuel cells include the following [8]:

Dohle et al. [9] present a model describing the fundamental operational characteristics of a DMFC. The model used is based on mass transport in the diffusion layers and membranes, as well as the reaction in the catalyst layers. Argyropoulos et al. [10] develop a thermal model based on energy conservation equations to predict the thermal behavior of DMFC stacks. Kulikovsky [11,12], meanwhile, develops analytical one-dimensional models for DMFCs to describe anodic and cathodic effects, as well as membrane permeation. The abovementioned approaches provide a deep insight into the microscopic processes of a DMFC. The application of these results for the modeling of DMFC systems is challenging, because the variables, that are required to calculate microscopic processes in a DMFC stack, can hardly be identified.

As the operational behavior of DMFCs is influenced by diverse, somewhat complex microscopic effects, it is effective to use statistical "black box" models to correlate relevant input and output variables [8]. In order to systematically determine the characteristic properties of DMFC stacks, a full factorial experimental plan that demands numerous experiments is often necessary. Applying the design of experiments (DOE) approach greatly reduces the measurement effort [8,13–16]. Using response surface methodology (RSM), the characteristic operational behavior of DMFC stacks can be analyzed as a response to the operating parameters. It is possible to describe the operational behavior of a stack with mathematical models which can be used, for example, to model complete DMFC systems.

In the literature, there are different studies that focus on the application of DOE methods and RSM for fuel cell characterization. Wahdame et al. [17,18] apply the DOE methodology to the optimization of a 5 kW fuel cell stack and present DOE applications in the field of fuel cells research. Carton et al. [19] employ DOE methods to estimate the influence of different flow field geometries on the voltage and current of a hydrogen fuel cell. Eccarius et al. [20] utilize DOE coupled with a mathematical model to quantify the factors affecting methanol crossover in a DMFC.

Silva et al. [21] apply RSM to describe the power density of a DMFC as a function of temperature, methanol concentration, air-flow rate, methanol flow rate, and relative air humidity. The conclusion of Silva et al. clarifies that the temperature, methanol concentration and air-flow rate are relevant factors that affect the power density of a DMFC, which is an important result for this work. Taymaz et al. [22] report on the optimization of the operating conditions of DMFCs by generating a quadratic model through RSM in terms of related independent variables, describing the current as a response. Xu et al. [23] carry out numerical simulations to identify a relationship between the methanol feed concentration and power density at a given current density. These mentioned models are suitable to predict the stack power and to perform simple calculations. To generate a model of a complete DMFC system the stack's permeation must be known. A publication of Zenith et al. [24] contains mathematical regression models to predict the methanol crossover in a DMFC. The model was developed in order to enable feedforward (sensorless) control of anodic concentration in DMFC systems.

To perform a model-based optimization of DMFC systems, it is necessary to predict the output parameters of the utilized DMFC stack, which are given as the combination of cell voltage, water permeation and methanol crossover, depending on the stack's operating point. These three values allow the calculation of thermal balances and mass balances so a complete water autonomous DMFC system, which is fed with pure methanol, can be modeled. Presently publications containing a sufficient data base for the modeling of a DMFC stack operated in a DMFC system are rare. Within this publication a set of regression models for a single DMFC stack describing the operating characteristics comprising its combination of cell voltage, methanol crossover and water permeation is developed. Accordingly this paper bridges a gap in the literature and exemplifies an efficient method of stack characterization as important tool in the ongoing development of DMFC stacks and systems.

A satisfactory set of regression models is able to correlate the abovementioned output parameters in terms of the given