CONTROL THEORY BASED MODELS FOR DYNAMIC SOFC OPERATIONS

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ABSTRACT

In order to optimise SOFC single cells with respect to maximum electrical efficiency and life expectancy, the relationships between material properties and working conditions of single cells and their electrical performance ought to be well understood. This contribution presents an interdisciplinary approach to modeling materials development by applying computational intelligence techniques of systems and control theory. Qualitative models are used to formalize expert knowledge about irreversible materials changes at the cathode/electrolyte interface. The resulting model enables simulations instead of time-consuming experiments. The contribution first introduces modelling techniques of control theory. A qualitative model for the startup of SOFC single cells is then developed. First results with respect to the development of SOFC stacks conclude the paper.

INTRODUCTION

Physical modelling is known on different levels of abstraction. On the atomic level, micro models are based on molecular dynamic equations (1). However, these methods are not applicable for structures as complex as the SOFC electrodes. The computational effort is too large for such complex systems.

Using grain structures instead of single atoms leads to the level of mesoscale models. These models consider diffusion laws for finite volume elements. Here, modelling of SOFC electrodes fails because important transport parameters are unidentified.

These two modelling approaches reflect the properties of the true system. They are constructed exclusively from prior knowledge and physical principles without any use of measurements of the system (2). A physical interpretation of all variables and constants is possible if the constants are known a priori.

Macro models constitute the third level of abstraction. The porous electrodes and the dense electrolyte of an SOFC are modelled as homogeneous layers. Equivalent circuit diagrams simulate these layers; standard circuit elements represent different processes. On the macroscale level, parameters lose their reference to the material microstructure.
Concerning the microstructure of an SOFC cathode, building a model based on chemical reaction equations fails because of the complexity of the interface reactions. In addition, even the elementary processes at the interface during SOFC operation and leading to the cathodic polarization losses are not completely understood. A great part of the expert knowledge is imprecise and only of a qualitative manner.

Conventional modelling techniques of materials science cannot use this knowledge, because it is not given by mathematical equations but by linguistic rules. These rules consist partially of qualitative and uncertain premises and conclusions.

This paper presents an interdisciplinary macroscale modeling approach that is able to combine qualitative expert knowledge with physical relationships and measured data. Computational intelligence techniques of systems and control theory allow to build a dynamic model of the microstructural formation of the cathode/electrolyte interface of SOFC single cells under the influence of the first electrical loading.

At first, the investigated SOFC materials and their startup behavior are introduced. General requirements of building a model are considered from a control and systems theoretical point of view. Modeling approaches of control theory for different fields are presented. Then, starting from qualitative expert knowledge, a nonlinear dynamic model of the microstructural changes during startup is developed.

MODELLING IN CONTROL THEORY

In natural sciences, control theory is known as an engineering science that deals with controlling technical systems. Actually, designing a controller is a principal task of control engineering, but not the only one. In many control applications, designing the controller demands less time than a more important element of control theory: building a mathematical model of the system to control.

Many controller design methods require a mathematical model that represents the behaviour of the system. And in many cases, an extensive analysis of that model and the systems dynamics precedes the actual controller design. The description "systems and control theory" meets these elements of control engineering.

Since systems and control theory is an independent engineering field, it deals with applications in a variety of other sciences. These are not limited to classic application areas like electrical, mechanical and process engineering. For instance, control engineering methods can also be adopted in economy and in ecological systems. Since any of these sciences uses its own particular modelling technique, this wide range of application fields has led to a great deal of modelling know-how in control engineering.

In control engineering, modelling is classified in two major methodologies: first principles modelling and system identification. From a modelling point of view, first principles models are desirable because they represent the system behaviour exactly. However, three difficulties are related to first principles modelling: Firstly, first principles modelling is impossible when physical relations of the system are not known. Secondly, even if the internal system structure is known completely, still some values of
parameters may be missing. And thirdly, in case a complete dynamic model can be built, it often can not be used for designing a controller because it is too complex. Many control design methods require a simple model that is a model with an order as low as possible.

Therefore, beside first principles modelling, system identification constitutes a major part of modelling activities in control theory. System identification allows to build a mathematical model based on experimental data. If the physical structure of the system is not known at all, a standard model structure is assumed and system identification determines parameters of that structure. Typical standard structures of control theory are linear transfer functions and nonlinear characteristic diagrams. Since the parameters of these models do not have any physical meaning, this modelling approach is known as black box modelling.

Consequently, first principles models can be designated white box models. In between, a wide diversity of modelling approaches combines physical laws with experimental data. Such techniques are characterized by the term grey box models.

These grey box models often have to cope with different sources of information. In addition to physical relations and experimental data, expert knowledge often constitutes an important portion of the knowledge about a system. However, representing that knowledge by mathematical equations is difficult. Since control engineers often have met this problem, modern techniques of artificial intelligence have entered control theory and have been enhanced there. As a result, now standard techniques for representing expert knowledge are available. If the expert knowledge contains uncertainty or if it is only qualitative knowledge, so called fuzzy models can be used for mathematical representation. Fuzzy sets model uncertain linguistic terms, for example “fairly hot” or “quite fast”. Numerical meanings of such terms may be determined either directly by an expert or in combination with experimental data. Since in many cases experimental data are necessary to find a numerical meaning of linguistic terms, fuzzy models are associated with “computational intelligence”, which also comprises neural networks, expert systems, genetic algorithms, and data mining.

To return to materials development: in other scientific fields, control theory has proven to be a connector that allows modelling techniques to cross borders between disciplines. It is the purpose of this contribution to show that modern modelling approaches of control theory can facilitate materials development for solid oxide fuel cells as well.

Since microscale models are hard to find for complex fuel cell systems, modelling is performed on a macroscale level. Qualitative expert knowledge is used to define a model structure. This model structure has some physical meaning, but model parameters have to be determined by experimental data. The next section introduces the application, the formation of the cathode/electrolyte interface of an SOFC.

**EXPERIMENTAL**

The SOFC single cells used in this work were based on a 150 μm thick 8YSZ substrate with a size of 50 x 50 mm², on which a Ni/8YSZ anode and a single layer cathode were screen printed using an EKRA Microtronic 2-K screen printing machine with optical...
positioning system. \( \text{La}_{0.8-x}\text{Sr}_{x}\text{MnO}_3 \) cathode pastes \((x=0: \text{stoichiometric - LSM}; x=0.05: \text{La-deficient - ULSM})\) were synthesized by calcination of appropriate compositions of \( \text{La}_2\text{O}_3, \text{Mn}_2\text{O}_3 \) and \( \text{SrCO}_3 \) mixtures, followed by grinding and mixing with organic binders. The sintering temperature was 1300°C. The active area of the electrodes was 35 x 30 mm\(^2\). Reference electrodes with 5 x 5 mm\(^2\) were also applied. The single cells were mounted into ceramic housings, cathode and anode were contacted by platinum and nickel meshes, respectively. Gold frames were used for sealing. The cells were operated under fully computer controlled stack-like conditions. Operating temperature was 950°C at ambient pressure with air as oxidant at the cathode and hydrogen as fuel at the anode with a humidity of 5%. Gas flow rates were 0.5 slm. The working electrodes of the cell were electrically loaded with an electronically controlled current sink. The open circuit voltage and the electrode polarizations can be measured by use of the reference electrodes. Electrical measurements are the only way to characterize the current state of the cell during operation. Details on the measurement set-up are given in (4).

**OPERATION OF SOFC SINGLE CELLS**

Figure 1 shows the temporal course of the cell voltage and the anodic and cathodic polarizations for a typical startup measurement. With increasing electrical load, the cell voltage first decreases sharply, but then – for constant current density – increases significantly. This phenomenon can be attributed completely to the cathodic losses, since the electric losses at the anode remain constant for constant current density. The reduction of the cathodic losses has been observed only during the first electric loading of the cells. Therefore, in the following, the startup process is referred to as cell activation. In (3), this behaviour was attributed to two processes causing microstructural changes at the cathode/electrolyte interface. The correlation between activation process and structural properties of the cathode/electrolyte interface is investigated in (5). The next section introduces a dynamic model that reproduces the measured behaviour of Figure 1.

![Figure 1. Activation of a single cell. Significant increase of the cell voltage and the cathode voltage for constant current density between 6 h and 40 h.](image-url)
QUALITATIVE MODELING OF SOFC ACTIVATION

The structure of the qualitative dynamic model is shown in Figure 2. During the startup only electrical data are measurable. Therefore the structure of the model is shown as an electrical equivalent circuit diagram. The measurable signals are the open circuit voltage $U_o$, the current density $j$ and the cell voltage $U_{cell}$. The difference between $U_o$ and $U_{cell}$ represents the losses under working conditions.

Two classes of losses can be distinguished. First, losses appearing both during startup and after a complete activation of the cell. These are static losses (part A in Figure 2) and additional dynamic losses caused by load changes (part B). And second, losses, which appear only during the first electrical loading of the cell (part C).

The model represents the static losses by a current/voltage characteristic, as it is shown in Figure 3a. This characteristic comprises the ohmic losses of the cell and the polarisation losses of cathode and anode. The dynamic behaviour of activated cells has to be modelled as well, because its time dependencies are in the same order of magnitude as those of the activation processes.

Figure 2. Structure of the qualitative dynamic model of the startup of SOFC single cells. The elements are correlated with the actual activation state.

Figure 3. a) Static current/voltage characteristic. b) Dynamic behaviour of the activated cell.

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Figure 4. Cell voltages during activation and operation for the load profile of Figure 1.

Figure 3b illustrates these dynamics. After load steps from a low to a high level, the cell voltage increases. This is caused by a decrease of the cathodic losses. In the equivalent circuit diagram this dynamic behaviour is represented by part B.

With parts A and B, the equivalent circuit of Figure 2 can simulate the behaviour of a completely activated cell for an arbitrary course of the current density. For example, the model can simulate the cell voltage that an activated cell would have shown when it had been loaded with the current density of Figure 1. Figure 4 shows the simulation result, it compares the measured voltage \( U_{\text{cell, startup}} \) to the simulated voltage \( U_{\text{cell, final}} \). This comparison clearly shows that the electric losses are much higher during the first electric loading. From Figure 1 it can be seen that these additional losses are caused by the cathode, the anode does not show any particular startup behaviour.

Therefore, the cathode losses during startup can be described as

\[
U_{\text{cathode, startup}}(j,t) = U_{\text{operation}} - U_{\text{cell}}
\]

with the notation of Figure 2.

Expert knowledge about what happens during startup allows to separate these losses into two parts. In

\[
U_{\text{cathode, startup}} = j(t)r_{\text{C/E}} + j(t)r_{\text{LZO}}
\]

\( r_{\text{C/E}} \) represents losses at the interface cathode/electrolyte (C/E) reduced during the startup because of an improvement of the interface. \( r_{\text{LZO}} \) describes losses caused by blocking phases like \( \text{La}_2\text{Zr}_2\text{O}_7 \). In time-discrete notation, the reduction of these resistances \( r_{\text{C/E}} \) and \( r_{\text{LZO}} \) can be expressed by equations of the form

\[
r_{k+1} = (1 - \alpha_k)r_k
\]

where \( r_k \) is the corresponding resistance at time step \( k \) and \( r_{k+1} \) will be the resistance after the next sampling interval. The factor \( \alpha_k \) (with \( 0 \leq \alpha_k < 1 \)) describes the reduction rate.
Qualitative process knowledge allows to define qualitatively the dependence of the factor \( \alpha \) on the current density and the current value of the resistance (6).

To represent that knowledge mathematically, linguistic rules have to be transferred into Fuzzy IF-THEN rules. For example: If there is no electric load, or if there is no resistance then microstructure does not change during this step, which means \( \alpha = 0 \) for the reduction rate. The following rules formalise this knowledge:

\[
\begin{align*}
\text{IF} & \quad j = 0 \quad \text{and} \quad r_{\text{C/E}} \quad \text{any} \quad \text{THEN} \quad \alpha = 0 \\
\text{IF} & \quad j \quad \text{any} \quad \text{and} \quad r_{\text{C/E}} = 0 \quad \text{THEN} \quad \alpha = 0
\end{align*}
\]

In the range of medium-sized current densities there are no specific rules for the reduction rate \( \alpha \). But it is possible to formalise qualitative correlations of the form

\[
\text{IF} \quad j = 0.6 \quad \text{Acm}^{-2} \quad \text{and} \quad r_{\text{C/E}} = 0.9 \quad \Omega \text{cm}^{-2} \quad \text{THEN} \quad \text{very fast reduction}
\]

As already stated in the introduction of this paper, imprecise terms like "very fast" can be handled by fuzzy set theory (7). In contrast to conventional set theory, where an element either belongs to a set or not, in a fuzzy set \( M \) each element \( x \in M \) is assigned a membership degree \( 0 \leq \mu_M(x) \leq 1 \) to the set. Elements with membership degree \( \mu_M(x) = 0 \) do not belong to the set, elements with \( \mu_M(x) = 1 \) belong completely to the set, and elements with \( \mu_M(x) < 1 \) belong to the set only to a certain degree. For example, the parameter \( \alpha \) of rule [6] can be represented by the fuzzy set in Figure 5.

When triangular fuzzy sets are used, these fuzzy sets can be represented by three parameters: their vertex and their left and right foot. The vertex is called "center", it marks the most possible value of the fuzzy set. The left and right foot represent the limits of the membership function.

For a given set of rules similar to rules [4]-[6], the left and right foot points of the fuzzy conclusions can be displayed in a nonlinear characteristic diagram. With an interpolation between several rules, a fuzzy characteristic results. Figure 6 shows the fuzzy characteristics for the reduction of the interface resistance and for the reduction of the LZO layer. Rule [6] with the lower and upper bound of the parameter \( \alpha_{\text{C/E}} \) is marked by the bold lines and circles in Figure 6a.
Figure 6. Upper boundary (grey) and lower boundary (white) of the reduction rate $\alpha_{_{CE}}$ for the interface resistance and the LZO-reduction rate $\alpha_{_{LZO}}$:
(a) $\alpha_{_{CE,k}} = f(j_k, r_{CE,k})$, (b) $\alpha_{_{LZO,k}} = f(j_k, r_{LZO,k})$.

RESULTS

The structures of the functions $\alpha_{_{LZO,k}}$ and $\alpha_{_{CE,k}}$ in Figure 6 are different. The LZO reduction begins at low current densities whereas the reduction of the interface resistance starts only at much higher current densities. The qualitative expert knowledge defines the shapes of the two characteristics, system identification and experimental data can be used to determine their exact numerical course. Furthermore, the initial resistances $r_{CE,0}$ and $r_{LZO,0}$ can be automatically computed from measured data. This combination of qualitative expert knowledge determining the model structure and system identification obtaining numerical parameters is a typical grey box modelling approach.

The resulting model simulates the behaviour of an SOFC single cell during the first electric loading. Since the simulation result can not be more precise than the knowledge used for modelling, a “fuzzy simulation” is obtained. The predicted cell voltage is illustrated in Figure 7a. Due to uncertainties in the fuzzy rules and imprecise initial conditions, the cell voltage can be predicted only qualitatively.

Figure 7. (a) Simulation of the cell voltage compared to measurement data of an SOFC single cell (LSM cathode). (b) Simulation of the internal – not measurable – resistances during the activation of an SOFC single cell (LSM cathode).
However, the comparison with the measured cell voltage in Figure 7a shows that the model prediction covers the measured behaviour. The model now allows to simulate the behaviour of the internal resistances that can not be measured during operation. Figure 7b shows the predicted LZO resistance and the improvement of the interface C/E for the load profile of Figure 4. Even though after sintering the LZO resistance is by a factor of five higher than $r_{CE}$, after some hours of operation the reduction of $r_{CE}$ becomes the dominating process.

**CONCLUSIONS**

A dynamic model of the activation of SOFCs was developed from expert knowledge and measurement data. The model reflects the uncertainties of the expert knowledge and thus not only covers the behaviour of one particular cell, but also allows to predict the behaviour of all cells produced with the same batch.

In cells with stoichiometric cathode composition $(La_0.8Sr_0.2)MnO_3$, the LZO layer decomposes during the first hours of operation, even for low current densities. But an activation behaviour can also be observed, when there isn’t any LZO layer, for example when cathodes with sub-stoichiometric composition $(La_{0.75}Sr_{0.2})MnO_3$ are investigated. The dynamic model shows that the cathode/electrolyte interface is improved for both cathode material types.

Operating conditions can be assumed to be homogeneous for single cells. However, in an SOFC stack, the fuel supply will be inhomogeneous over the stack plane. As a consequence, the current densities will be locally different as well. At the gas inlet, where pure H$_2$ is supplied, the local current density will be at its maximum, whereas at the gas outlet, where the fuel contains 80% H$_2$O, the local current density will be very low. With the dynamic model of the activation, it is now possible to simulate the impact of an inhomogeneous current density distribution on the activation of a stack. First results have been presented in (8). From these simulations, it can be concluded that low current densities, which may be apparent at the stack outlet, cannot enlarge the triple phase boundary within an acceptable time period. The local operating conditions can also be tested experimentally by supplying a specific fuel gas mix of H$_2$ and H$_2$O and a specific current density. Measurements have proven that for the conditions at the stack outlet with high fuel utilization and low currents, a complete cell activation is not possible.

The present study shows that qualitative modelling techniques – known in systems and control theory – open new horizons for materials development, since they allow to incorporate qualitative expert knowledge in combination with measurement-based information.

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