SYSTEM IDENTIFICATION:
A NEW MODELLING APPROACH FOR SOFC SINGLE CELLS

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ABSTRACT

Due to the great number and complex nature of physico-chemical processes, a comprehensive model describing SOFC single cell operation is at present not available. System identification, a modelling approach from control theory is proposed. Instead of inferring models from physical laws, the method is based on experimental data to build a mathematical model. Model parameters may subsequently be related to physical processes in the cell. The method is carried to the point of pre-identification of SOFC electrochemical impedance spectroscopy data. A new technique has been developed for calculating the distribution of relaxation times directly from the data. No equivalent circuit has to be assumed. In addition the method yields a higher resolution of dynamical processes than non-linear least squares curve fit. Kramers-Kronig transformation of impedance data was used to calculate the ohmic resistance of the electrolyte and the total polarization resistance of the cell.

INTRODUCTION

In order to optimize the SOFC single cell with respect to maximum electrical efficiency and long term stability the interaction between the cell parameters, i.e. its material properties and operating conditions, and its electrical performance ought to be well understood. Modelling is usually done by splitting up the system into sub-systems, whose properties are well established from physical laws. The sub-models are combined to obtain a model of the whole system. However, comprehensive models describing SOFC single cell operation are at present not available because of the high complexity of concurring physico-chemical processes. In this paper, an alternative to theoretical modelling based on physical laws is presented: system identification. This approach originates from control theory. It deals with the problem of inferring mathematical models of dynamical systems based on observed data from the systems (1). With this approach, there is in principle no need for a priori knowledge of the physical processes in the cell. In other words, the cell is regarded as a technical process in a "black box" (Fig. 1).

The input-output data of SOFC operation are recorded by electrical measurement. Well-known examples of such input-output data are electrochemical impedance spectra, I/V-characteristics and long term measurements. Possible input signals are current and impedance distortion applied to the system, measured output signals are cell voltage, voltage losses and impedance data. Cell parameters are all kinds of properties that influence cell performance: materials characteristics (e.g. composition and porosity of electrode layers),...
production parameters, working conditions like temperature, gas composition, etc., and material parameters obtained from post-test analysis (Fig. 1).

System identification is an iterative method that consists of three steps: pre-identification, model estimation and model validation (Fig. 2). During pre-identification, the data from the system under investigation are subjected to numerical analysis in order to make it suitable for modelling and a corresponding model structure is chosen. In the next step, model estimation, the parameters of the model are determined by suitable parameters estimation methods. It then remains to test whether this model is "good enough". Such tests are known as model validation. If the model does not relate to observed data or if the dynamical range of the model is to be extended, we must go back and revise the three steps of system identification. The obtained model represents information about the underlying physical processes as long as they can be distinguished in terms of time constants. If an adequate model can be found, changes in the physical parameters of the cell can be related to changes in the formal parameters of our model. Once a relationship is established, the effect of cell parameter changes on cell performance can be predicted.

The scope of the present paper is an initial step into system identification of SOFC single cell operation. Fig. 3 shows the wide range of time constants at which physical processes are observed together with some examples of these processes. Different measurement techniques are employed to cover this time scale. At present, electrochemical impedance
spectroscopy (EIS) data are the only type of data used for system identification, hence the model covers the corresponding time scale only. A method for the pre-identification of impedance spectra will be presented that yields more information from the data than non-linear least squares curve fit.

**EXPERIMENTAL**

The electrical impedance of planar SOFC single cells (30 μm porous LSM cathode, 200 μm dense 8YSZ electrolyte, 30 μm porous Ni-8YSZ cermet anode) with an electrode area of 1 cm² was measured under realistic working conditions (2). The maximum frequency range was from 1 mHz to 1 MHz. A SOLARTRON 1260 impedance frequency response analyzer was used. The data were logarithmically sampled with 10 points per decade. All experiments were conducted as series of impedance measurements in which one cell parameter, e.g. temperature, gas composition, current density, fuel utilization, etc. was varied. Impedance spectra are shown in (3).

**PRE-IDENTIFICATION OF IMPEDANCE DATA**

It is often questionable to use equivalent circuit models for the evaluation of EIS data from SOFC operation because of the great number of physical processes contributing to the overall impedance. Due to overlap in the frequency domain, these processes can hardly be separated. Therefore, a method was developed to extract information from EIS data which is useful for modelling. The method allows to calculate a distribution function of the time constants of polarization processes directly from impedance data without using physical knowledge about the system.

**Distribution of Polarization Processes**

A polarization process in an electrochemical system is commonly described by a simple equivalent circuit, e.g. an ohmic resistance in parallel to a capacitance or a constant phase element. In the former case this corresponds to a single time constant \( \tau_0 = RC \), in the latter to a certain distribution of time constants (4). A more precise representation of a
polarization mechanism can be achieved by allowing the time constants to be arbitrarily distributed. In order to describe this distribution mathematically, a distribution function of polarization processes \( g(f) \) is introduced (5). Fig. 4a shows an example of \( g(f) \) for two RC-elements. The function exhibits impulses at the time constants \( \tau_i = R_{pol,i}C_i \). "Non-ideal" polarizations (fig. 4b) can be described by a distribution of time constants with a central frequency and a characteristic shape and width. The area enclosed by the peak corresponds to its polarization resistance \( R_{pol,i} \).

**Mathematical Realization**

Consider a serial connection of RC-elements. Let \( R_{pol,k} = \gamma_k R_{pol} \) be the ohmic resistance and \( \tau_k \) the relaxation time of the \( k \)-th RC-element. \( R_{pol} \) is the total ohmic resistance of the circuit. The impedance is

\[
Z_{pol}(\omega) = \sum_{k=1}^{N} \frac{R_{pol,k}}{1 + j\omega \tau_k} = R_{pol} \sum_{k=1}^{N} \frac{\gamma_k}{1 + j\omega \tau_k} ; \quad \sum_{k=1}^{N} \gamma_k = 1 ; \quad f^2 = -1 \quad [1]
\]

Instead of a finite number of RC-elements we now assume an infinite number with time constants reaching continuously from 0 to \( \infty \).

\[
Z_{pol}(\omega) = R_{pol} \int_{0}^{\infty} \frac{\gamma(\tau)}{1 + j\omega \tau} d\tau ; \quad \int_{0}^{\infty} \gamma(\tau) d\tau = 1 \quad [2]
\]

Any given electrical circuit can be transformed into [2], hence the approach is generally valid (4). \( \frac{\gamma(\tau)}{1 + j\omega \tau} d\tau \) specifies the fraction of the overall polarization with relaxation times between \( \tau \) and \( \tau + d\tau \). We wish to obtain \( \gamma(\tau) \) from \( Z_{pol}(\omega) \). According to the Kramers-Kronig transformations (6), real and imaginary part of the impedance contain the same amount of information and therefore, it is sufficient to only use the imaginary part of the impedance

\[
\text{Im} \{ Z_{pol}(\omega) \} = Z_{Im}(\omega) = -R_{pol} \int_{0}^{\infty} \frac{\omega \tau}{1 + (\omega \tau)^2} \gamma(\tau) d\tau. \quad [3]
\]

Since the impedance data are logarithmically sampled the variables have to be substituted as follows: \( x = \ln \frac{\omega}{\omega_0} ; \quad y = \ln \omega \tau ; \quad dy = \frac{\omega}{\tau} d\tau \). The impedance data can then be expressed in the form of a convolution product

\[
Z_{Im}(x) = -\frac{R_{pol}}{2} \int_{-\infty}^{\infty} \text{sech}(y) g(y-x) dy = -\frac{R_{pol}}{2} \text{sech}(x) * g(x) \quad [4]
\]
with

$$\text{sech}(y) = \frac{2}{e^y + e^{-y}}; \quad g(y - x) = \gamma(\tau)x.$$  \[5\]

$Z_{I_m}(x)$ is now evaluated at the data samples: $Z_{I_m}(x) \rightarrow Z_{I_m}(x_k); x = x_1, \ldots, x_N$ where $N$ is the number of samples. We convert [4] into an algebraic product by Fourier transformation (1) and calculate $\tilde{g}(n)$ by element-wise division:

$$\tilde{z}(n) = -NT\frac{R_{pol}}{2} \tilde{g}(n) \cdot \tilde{s}(n) \Rightarrow \tilde{g}(n) = -\frac{2}{NTR_{pol}} \frac{\tilde{z}(n)}{\tilde{s}(n)}.$$  \[6\]

Here $\tilde{z}(n), \tilde{s}(n), \tilde{g}(n)$ mean the Fourier transform of $Z_{I_m}(x), \text{sech}(x)$ and $g(x)$, respectively. $T = \frac{1}{N-1}\ln\frac{\omega_{\text{max}}}{\omega_{\text{min}}}$ is the sample interval. Inverse Fourier transform of $\tilde{g}(n)$ then gives the distribution function

$$g(f) = g(x) = \mathcal{F}^{-1}\{\tilde{g}(n)\}.$$  \[7\]

The method was developed with the numerical analysis software SCILAB. It was tested with synthetic impedance data generated from simple equivalent circuits. Fig. 5a shows an impedance spectrum calculated from a circuit with six RC- and RQ-elements with parameter values in table 1. Q denotes a constant phase element (CPE) with the admittance $Y = Y_0(j\omega)\gamma$; $0 < n \leq 1$ (4). The impedance spectrum has a low-frequency (< 100 Hz) and a high frequency arc (> 100 Hz). Polarization processes within these arcs are hard to separate with non-linear least squares curve fit due to overlap and because of the fact that equivalent circuits are ambiguous, i.e. one and the same impedance spectrum may be obtained from different circuits (4). In contrast, the distribution that was calculated from the synthetic data exhibits distinct peaks at the given frequencies (5b). As expected the obtained distribution broadens with decreasing $n$. Polarizations within the particular arcs are well separated. This result is entirely independent of equivalent circuit models. No a priori assumptions about the system have to be made to obtain the distribution.

**Evaluation of the Distribution Function**

Each peak $i$ in $g(f)$ represents a polarization process and is characterized by its peak frequency $f_{0,i}$, the area enclosed by the peak corresponding to its polarization resistance $R_{pol,i}$ and by its half-width $\omega$ relative to the peak height. These parameters were calculated by non-linear regression of a set of model peaks to the distribution using the Marquardt-Levenberg fit algorithm. The values obtained from the fit and the relative error of fitted to given values (r.e.$f_{0,i} = \frac{\text{r.e.}f_{0,i}}{f_{0,i}}$) are shown in Table 1. The peak frequency can be

<table>
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<th>given values</th>
<th>values obtained from peak fit</th>
</tr>
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<td>$R_{pol,i}/\Omega$</td>
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**Table 1:** Parameters of synthetic data in comparison to parameters calculated from peak fit
determined very precisely whereas the error in $R_{pol,i}$ is larger and depends on the particular function chosen for the respective model peak. The relationship between $n$ and $w$ has not yet been investigated closely, however, $n$ can probably be estimated when $w$ is known.

**Kramers-Kronig Transformation of EIS Data**

The impedance data was analyzed under the assumption that it consists of a dispersive and a non-dispersive (ohmic) part: $Z(\omega) = Z_{pol}(\omega) + R_0$. It was assumed that $R_0$ is responsible for the voltage drop in the electrolyte whereas all polarization losses are lumped in $Z_{pol}$. $R_0$ and the total polarization resistance $R_{pol}$ were determined by Kramers-Kronig (KK) transformation of impedance data. The real part of the impedance was calculated from the imaginary part by discrete integration using a special form of the KK-transformation (7).

$$Z_{Re,KK}(\omega) = Z_{Re}(\omega) - R_0 = \frac{2\omega}{\pi} \int_0^\infty \frac{v}{v^2 - \omega^2} Z_{Im}(v) - Z_{Im}(\omega) \, dv$$

$$\approx \frac{2\omega_k}{\pi} \sum_{k=1}^N \frac{\omega_k}{\omega_k^2 - \omega^2} Z_{Im}(\omega) - Z_{Im}(\omega_k)$$

[8]

In contrast to (7), the removable singularity at $v = \omega$ was handled by taking the mean of the adjoining values as the integrand value at $v = \omega$, and not by omitting this value. The KK-transformations were tested with synthetic data. The relative error of synthetic data and its KK transforms was $< 0.05 \%$. 

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**Figure 5:** a) Impedance spectrum of synthetic data (frequencies are in Hz) and b) corresponding distribution function $g(f)$ in arbitrary units.
Figure 6: Kramers-Kronig transform of impedance data

\( R_0 \) was calculated by taking the mean of the differences \( Z_{Re}(\omega_k) - Z_{Re,KK}(\omega_k) \) at each sample. \( R_{pol} \) was determined by a special form of the KK transformation that is obtained when evaluating [8] for \( \omega \to \infty \). \( R_{pol} \) is of particular interest because the distribution function \( g(f) \) is normalized so that the area comprised by \( g(f) \) equals \( R_{pol} \). Fig. 6 shows a comparison of actual impedance data and its KK-transform \( Z_{Re,KK}(\omega) \) plotted versus the logarithmic frequency. The cell was operated at \( T = 950 \, ^\circ C \) in pure hydrogen and with air as oxidant at a current load of 500 mA/cm\(^2\). The vertical shift between calculated and measured real part of the impedance corresponds to the electrolyte resistance \( R_0 \) (7).

The above result implies that the electrochemical system exhibits linear behaviour, i.e. it can be represented by the distribution \( g(f) \), and that \( R_0 \) and \( R_{pol} \) can be determined with reasonable precision.

Extrapolation

The calculation of \( \tilde{z}(n) \) in [6] and the evaluation of [8] requires an infinite range for \( \omega \to 0 \) and \( \omega \to \infty \). The limited measurement range causes an error, because \( Z_{Im}(\omega) \) is not zero at the edges of the measurement range \( (\omega = \omega_{min}, \omega_{max}) \). However, \( Z_{Im}(\omega) \) normally tends to zero and thus can be extrapolated. This was done on the assumption that on the edges only one polarization process is still active. In this case, \( Z_{Im}(\omega) \) can be approximated by a straight line in the plot of \( \log |Z_{Im}| \) versus \( \log \omega \) (7). Very "slow" processes \( (\omega \ll \omega_{min}) \) contribute to \( R_0 \). Very "fast" processes \( (\omega \gg \omega_{min}) \) are not measured and not included in \( R_{pol} \). The extrapolation is carried to the point where \( Z_{Im}(\omega) \) is so close to zero, that the error can be neglected. This is usually reached over several frequency decades, e.g. at \( 10^{-6} \) Hz and \( 10^{12} \) Hz. Inductive loops in the impedance data at low frequencies are taken into account by the extrapolation procedure. Inductive loops at high frequencies were attributed to the electrical wiring and measurement devices and therefore cut off. Fig. 6 shows impedance data and its extrapolated imaginary part \( Z_{Im,Expol} \) plotted versus logarithmic frequency. The error in the computation of \( g(f) \) and \( R_0 \) was significantly reduced by this procedure.
RESULTS AND DISCUSSION

Fig. 7a shows actual impedance data measured at a SOFC single cell. An inductive loop is observed at frequencies between 10 mHz and 1 Hz followed by a broad depressed semi-circle between 10 and $10^4$ Hz.

![Impedance data graph](image)

Figure 7: a) Impedance data (frequencies are in Hz) and b) corresponding distribution function $g(f)$ in arbitrary units

The corresponding distribution of polarization processes is shown in Fig. 7b. 11 peaks are visible. The peak parameters were determined by the peak fit method described above and are shown in Table 2. The inductive loop falls into three processes (1-3). There are three processes at intermediate frequencies (4-6) and 5 processes at high frequencies (7-11). The broad peak (11) is caused by the flat line in the impedance spectrum observed at high frequencies. $R_{pol,i}$ of the particular peak indicates the contribution of the corresponding process to the overall polarization $R_{pol}$. For instance, the processes of the inductive loop cause $\sum R_{pol,1-3}/R_{pol} = 7.2\%$ of the polarization. The electrolyte resistance was determined as $R_0 = 0.14908 \, \Omega$. The theoretical value calculated from bulk conductivity

<table>
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<th>i</th>
<th>$f_{0,i}$/Hz</th>
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Table 2: Parameters obtained from peak fit
data is 0.140 Ω at $T = 950 \ ^\circ C$ and is thus in reasonable agreement.

In order to attribute physical processes to the observed peaks, impedance measurements series were conducted in which one cell parameter was varied. The influence of the parameter change on the distributions was studied. For a detailed discussion, see (3).

**CONCLUSIONS**

A numerical method for the evaluation of impedance spectra was presented. The method allows to calculate the distribution of polarization processes directly from the data, without the use of equivalent circuit models and non-linear curve fit. The feasibility of the method was shown with synthetic data. The method is able to separate processes that overlap in the impedance spectrum. KK transformations were used to determine the electrolyte resistance $R_0$ and the total polarization $R_{pol}$. Ongoing work focuses on the investigation of special features in the impedance spectra like inductive loops and diffusion lines (e.g. Warburg impedances) and their effect on the distribution functions.

![Diagram](image)

**Figure 8: Model-aided materials design of SOFC single cells**

Parameters obtained from a series of distribution design functions can be used for system identification of SOFC. The long term aim of the studies is a comprehensive model of the SOFC that simulates how the cell parameters affect performance and long term stability of the cell (Fig. 8). The model will provide a frame work for a systematic and consistent description of cell parameter dependencies. Furthermore, a deeper understanding of the SOFC in terms of system theory provides us with starting points for the integration of physical sub-models into a comprehensive description of the cell.

**REFERENCES**