ABSTRACT

System identification, a method used in control theory for modelling complex dynamical systems, is applied to the identification of SOFC oxygen reaction parameters. The present approach is based on distributions of relaxation times, which are the basic quantity of interest in electrochemical impedance data analysis. By a newly implemented deconvolution method, characteristic distribution patterns are directly computed from impedance spectra measured at single cells under realistic working conditions. In contrast to non-linear least squares curve fit of equivalent circuit models, no a priori circuit choice has to be made. The excellent resolving capacity allows to untangle impedance contributions of up to three physically distinct processes within one frequency decade. The analysis procedure is illustrated by a reaction model which describes the adsorption of oxygen on the electrode surface and the incorporation of oxide ions into the electrolyte. Based on the reaction model, the influence of varying the cell’s operating conditions on the parameters of the relevant peaks in the distributions is simulated. The kinetics of the reaction steps are then identified using distributions of relaxation times calculated from the impedance spectra measured at the corresponding operating conditions, thus providing a strong tool for SOFC diagnosis.

INTRODUCTION

Comprehensive models describing SOFC performance in terms of the cell’s materials parameters and operating conditions are at present not available. However, these models are required to optimize the SOFC with respect to maximum electrical efficiency, long term stability and operation robustness. The lack of suitable models is caused on the one hand by the very high complexity of concurring physico-chemical processes present in cell operation and on the other hand by the limited information available from electrical measurements and materials analysis techniques. The number of parameters of a particular model is often greater than the number of parameters that can be identified unambiguously from the experimental data. The present study deals with the interpretation of electrochemical impedance spectroscopy (EIS) data measured at single cells under realistic working conditions in terms of physical sub-models. By a newly implemented deconvolution method (1, 2), the distribution of relaxation times and relaxation amplitudes of physical processes and loss factors is computed directly from the experimental impedance data, yielding a much higher frequency resolution than the non-linear least squares curve fit method. Based
on the distributions, a mathematical model describing SOFC operation is established. This model contains no structural information about the physical nature of the system under investigation. In other words, the cell is regarded as a black box (fig. 1) having a specific output/input-(transfer)-behaviour that depends on the cell's materials parameters and operating condition. This approach is known as system identification (3).

Once characteristic transfer functions have been validated, the cell's performance in response to changes in operating conditions, e.g. electrical load or temperature, can be predicted providing a means to operation management. Simulation of cell performance for different operating conditions could also be used for the operation management of whole stacks. Furthermore, distributions from impedance data are characteristic patterns of single cells and can be used as "finger prints" for quality control after cell production.

![Figure 1: SOFC operation as a "black box"-process](image)

For further improvement of SOFC performance, physical models of the processes in the cell are needed. These can be incorporated into the theoretical model and be identified from the distribution patterns if adequate model structures yielding an impedance expression are at hand. As an example we examine the electrochemical performance of the cathode/electrolyte interface which is one of the main factors determining the electrical efficiency of the cell. Although a large number of studies on mass and charge transport in SOFC electrodes has been conducted there is still considerable disagreement concerning the exact nature of the underlying reaction mechanisms. However, only if the electrochemical reaction mechanisms are well understood and the corresponding kinetic rate constants are known as a function of operating conditions and cell materials parameters, a well-directed improvement of SOFC electrodes can be carried out.

The present study illustrates how physical sub-models can be incorporated into the mathematical model and presents a general strategy for the determination of kinetic rate constants by comparing distribution functions from measurements and from simulations. As a practical example, the adsorption and reduction of oxygen at the cathode/electrolyte interface is modeled using an impedance expression from (4).

**EXPERIMENTAL**

The electrical impedance of planar 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. A SOLARTRON 1260 impedance frequency response analyzer was used. The ac signal was 5 mA with a bias current of 5 mA for the case of open circuit conditions. The maximum frequency range was from...
10 mHz to 1 MHz. The data were logarithmically sampled with 10 points per decade. The impedance was measured over the working electrodes as well as from working electrode to reference electrode on the anode and on the cathode side respectively. The cell testing setup and the electrode configuration we used is described in detail in (5). All experiments were conducted in series of impedance measurements in which one cell parameter, e.g. temperature, gas composition, current density, fuel utilization, etc. was varied. Typical impedance spectra are shown in (6).

**METHODOLOGY**

The basic quantity of interest in electrochemical impedance spectra is not the impedance data itself but the underlying distribution of relaxation times and relaxation amplitudes representing the loss processes in the cell. EIS data are commonly interpreted in terms of electrical equivalent circuit models. These models can be ambiguous and therefore misleading because of the great number of physical processes in SOFC operation (fig. 2). Their respective impedance contributions overlap in the frequency domain and can hardly be separated. Therefore, a numerical method was developed in order to extract more information from EIS data. The method allows to calculate the distribution of relaxation times and amplitudes directly from impedance data without any a priori assumptions about the internal structure of the system in form of equivalent circuit models.

![Physical vs Mathematical Equivalent Circuit Models](image)

**Figure 2:** Interpretation of EIS data in terms of (a) squares curve fit and (b) distributions of relaxation times. Equivalent circuit models are in general too coarse to allow a physical interpretation of single processes whereas the distribution function shows a much higher frequency resolution of physical processes.

**Principle**

A Debye polarization process is fully characterized by its time constant $\tau_0$ and its polarization loss $R$. In an equivalent circuit model, this process is represented by an RC-element, i.e. an ohmic resistance $R$ in parallel to a capacitance $C$ with $\tau_0 = RC$. Certain processes with relaxation times that are symmetrically distributed around a main value can...
be described by a parallel combination of an ohmic resistance and a constant phase element $Q$ \( (7) \). When choosing an equivalent circuit, one assumes a certain number and types of dispersion processes in the cell which is often not apparent in the form of the spectrum. An alternative to this indirect approach is to use an arbitrary distribution of relaxation times. This corresponds to a "general" equivalent circuit consisting of an infinite number of "differential" RC-elements in series (fig. 2b). Within this mathematical description the measured impedance $Z$ is expressed by an integral equation containing the distribution function $\gamma(\tau)$.

$$ Z(j\omega) = R_0 + Z_{pol}(j\omega) = R_0 + R_{pol} \int_0^\infty \frac{\gamma(\tau)}{1 + j\omega\tau} d\tau; \quad \int_0^\infty \gamma(\tau) d\tau = 1 \quad [1] $$

$R_0$ represents the ohmic part and $Z_{pol}$ the polarization part of $Z$, $R_{pol}$ is the total polarization resistance. The expression $\frac{\gamma(\tau)}{1 + j\omega\tau} d\tau$ specifies the fraction of the overall polarization with relaxation times between $\tau$ and $\tau + d\tau$. This implies that the area under each peak equals the polarization resistance of the corresponding loss mechanism.

We wish to obtain the distribution function directly from $Z_{pol}(\omega)$. Logarithmic variable substitution transforms \([1]\) into a convolution equation which can be solved by Fourier transformation. The procedure is described in detail in (8). It produces a distribution function $g(x)$ with one value per impedance data sample. Here $x$ denotes the logarithmic frequency $x = \ln \omega$ with $\omega_0$ as an arbitrary normalisation frequency. An ideal RC-element is represented in $g(x)$ by a Dirac impulse

$$ g_{RC}(x) = R_{pol,\text{RC}} \delta(x - x_0) \quad [2] $$

at the respective relaxation time $\tau_0 = \frac{1}{\omega_0} e^{-x_0}$. In principle, the frequency resolution of RC-processes is infinitely high in the distribution function. In real systems, the numerical procedure does not yield Dirac impulse functions, because the impedance is only available at discrete data points within a limited frequency range. However, processes of real systems often show a distributed behaviour by themselves due to inhomogeneous parameter distributions of the underlying processes that can be approximated by an RQ-element. An RQ-element shows a peak with increasing width and decreasing height as its exponent $n$ departs from unity \((7)\).

$$ g_{\text{RQ}}(x) = \frac{R_{pol,\text{RQ}}}{2\pi} \frac{\sin((1-n)\pi)}{\cosh(n(x - x_0)) - \cos((1-n)\pi)} \quad [3] $$

The area under the peak is independent of $n$ and equals $R_{pol,\text{RQ}}$. For $n \rightarrow 1$ this expression approximates the Dirac-impulse. The exponent $n$ can be determined from the half-width of the peak in the distribution. The half-width in frequency decades is given by

$$ h_g = \frac{1}{n \ln 10} \arccosh[2 - \cos((1-n)\pi)]. \quad [4] $$

**Evaluation of experimental data**

Fig. 3 shows impedance data measured at a single cell under realistic operating conditions. The distribution functions calculated from this data is shown in fig. 4. Whereas...
Figure 3: Impedance data (solid symbols denote decades of frequency) measured from 10 mHz to 100 kHz. The data was extrapolated and submitted to Kramers-Kronig transformation. From the distribution function, the impedance spectrum was reconstructed using the peak parameters.

The polarization processes overlap in the impedance curve, several processes can be clearly distinguished in the distribution. Each process is represented by one or several peaks in the distribution function. The peaks are evaluated by a non-linear regression fit procedure using a set of model peaks. The characteristic parameters of the model peaks are the frequency $f_{0,i}$, the height $g(f_{0,i})$, the area $R_{po,i}$, and their half-width $h_{g,i}$. These values as calculated from the distribution are shown in table I.

Figure 4: Distribution function $g$ calculated from the impedance data in fig. 3. The model peaks are denoted with numbers.
Table I: Parameters obtained from peak fit

| i | \( f_0 / \text{Hz} \) | \( R_{pol,i} / \Omega \) | \( h_{g,i} / \text{d.f.} \) | \( n_{\text{apparent},i} \) | \( n_{\text{real},i} \) |
|---|-----------------|----------------|----------------|----------------|----------------|
| 1 | 0.11597         | 0.38705        | 0.666          | 0.800          | 0.970          |
| 2 | 1.28520         | -0.03793       | 0.280          | 0.905          | 1.000          |
| 3 | 4.68900         | 0.08594        | 0.470          | 0.850          | 0.900          |
| 4 | 31.9507         | 0.07132        | 1.004          | 0.718          | 0.818          |
| 5 | 100.138         | 0.04451        | 0.388          | 0.875          | 0.975          |
| 6 | 480.452         | 0.04423        | 0.278          | 0.913          | 0.975          |
| 7 | 2610.36         | 0.13739        | 0.880          | 0.745          | 0.900          |
| 8 | 29428.6         | 0.01229        | 0.442          | 0.863          | 0.863          |
| 9 | 164097          | 0.01175        | 0.790          | 0.770          | 0.770          |
| \( \Sigma \) | -               | 0.75655        | -              | -              | -              |

Based on the half-widths of the peaks, the exponents \( n_{\text{apparent},i} \) of the corresponding RQ-processes were estimated. The impedance was then reconstructed from the peak parameters in table I. Due to loss of frequency resolution because of the limited frequency range, the values \( n_{\text{apparent},i} \) are in general too low and had to be adjusted to \( n_{\text{real},i} \). The original spectrum and the spectrum computed from the peak parameters then show excellent agreement (fig. 3) thus proving that the peak parameters in table I are correct.

**OXYGEN REDUCTION MODEL**

The peak parameters are the relevant dynamic constants of the impedance and can be used to calculate the transfer function of the system. This is done most conveniently in form of a state space model [5].

\[
\begin{pmatrix}
    \dot{u}_1 \\
    \dot{u}_2 \\
    \dot{u}_3 \\
    \vdots \\
    \dot{u}_N
\end{pmatrix} =
\begin{pmatrix}
    -f_{0,1} & 0 & 0 & \cdots & 0 \\
    0 & -f_{0,2} & 0 & \cdots & 0 \\
    0 & 0 & -f_{0,3} & 0 & \cdots \\
    \vdots & \vdots & \vdots & \ddots & \vdots \\
    0 & 0 & 0 & \cdots & -f_{0,N}
\end{pmatrix}
\begin{pmatrix}
    u_1 \\
    u_2 \\
    u_3 \\
    \vdots \\
    u_N
\end{pmatrix} +
\begin{pmatrix}
    C_1^{-1} \\
    C_2^{-1} \\
    C_3^{-1} \\
    \vdots \\
    C_N^{-1}
\end{pmatrix}
\]

\[
u = (1 1 1 \ldots 1) \cdot (u_1 u_2 u_3 \ldots u_N)^T + R_0 \cdot i
\]

\[
\begin{pmatrix}
    \dot{u}_1 \\
    \dot{u}_{dl} \\
    \dot{u}_{ads} \\
    \dot{u}_4 \\
    \vdots \\
    \dot{u}_N
\end{pmatrix} =
\begin{pmatrix}
    -f_0 & 0 & 0 & \cdots & 0 \\
    0 & -\frac{1}{R_0 C_{dl}} & 0 & \cdots & 0 \\
    0 & 0 & -\frac{1}{R_0 C_{ads}} & \frac{1}{R_0 + \frac{1}{R_{ads}}} & \cdots \\
    \vdots & \vdots & \vdots & \ddots & \vdots \\
    0 & 0 & 0 & 0 & -f_4
\end{pmatrix}
\begin{pmatrix}
    u_1 \\
    u_{dl} \\
    u_{ads} \\
    u_4 \\
    \vdots \\
    u_N
\end{pmatrix} +
\begin{pmatrix}
    C_1^{-1} \\
    C_{dl}^{-1} \\
    C_{ads}^{-1} \\
    \vdots \\
    C_N^{-1}
\end{pmatrix}
\]
\[ u = (1101 \ldots 1) \cdot (u_1 u_2 u_3 \ldots u_N)^T + R_0 \cdot i \]  

**Figure 5:** (a) Generalized equivalent circuit model corresponding to [5] and (b) integration of a physical sub-model [7]. Both circuits yield the same impedance.

State space models originate from control theory and are a general concept for treating linear systems (3, 4). In the model presented here, each peak in \( g \) is represented by an RC-element with the voltage \( u_i \) as the state variable. The current \( i \) is the input variable and the voltage \( u = u_1 + u_2 + \ldots + u_N \) is the output variable. The impedance of the system is easily computed with methods from control theory. Because this approach deals with linear systems only, constant phase behaviour cannot be treated in state space form. All exponents are assumed to be unity. However, the physical models considered here do not take into account constant phase behaviour. The state space form is convenient because sub-matrices in the state space model can be replaced without changing the overall impedance. This is illustrated in fig. 5b: the second and third RC-element of the general equivalent circuit are substituted by a circuit representing a physical sub-model which describes the oxygen reduction at the cathode/electrolyte interface. The actual values of the circuit elements in the different sub-matrices are easily calculated by algebraic methods from the values of the general model and vice versa.

Mitterdorfer investigated the oxygen reduction mechanism of the Pt, O2(g)|YSZ system and developed a state space model for heterogeneous electrode reaction mechanisms that allows to treat the steady state and frequency response behaviour within a unified formalism (4). The model accounts for dissociative adsorption of oxygen on the Pt surface and a two-electron transfer step near the triple phase boundary.

**Figure 6:** (a) \( Z_f \) and total impedance \( Z \) calculated for \( R_t = 0.5 \) \( \Omega \), \( R_{ads} = 1 \) \( \Omega \), \( C_{ads} = 1 \) mF, \( C_{di} = 100 \) \( \mu F \) and (b) corresponding distribution functions
\[
\begin{align*}
O_2 + 2s &\leftrightarrow 2O_{ad} \quad \Rightarrow \quad k_{ads}P_{O_2}[s]^2 = k_{des}[O_{ad}]^2 \quad [9] \\
O_{ad} + 2e^- + V_0^\infty &\leftrightarrow O_0^s + s \quad \Rightarrow \quad k_{red}[O_{ad}][V_0^\infty] = k_{ox}[O_0^s][s] \quad [10]
\end{align*}
\]

where \([s]\) is the concentration of vacant oxygen surface sites, \([O_{ad}]\) the surface concentration of adsorbed oxygen and \(N_0\) the surface density of active oxygen sites; \(k_{ads}\) and \(k_{des}\) are the rate constants for adsorption and desorption of molecular oxygen; \(k_{ox}\) and \(k_{red}\) are the rate constants for the charge transfer to the adsorbed oxygen; \([V_0^\infty]\) represents oxygen vacancies in YSZ and \([O_0^s]\) denotes occupied oxygen lattice sites in YSZ.

The evaluation of the mass and charge balances for these basic reactions leads to a non-linear state-space representation of the system with \([O_{ad}]\) as the state variable. Linearisation gives an expression for the "Faradaic" impedance \(Z_F\) which describes the oxygen reduction dynamics (4).

\[
Z_F(j\omega) = R_t \left[ 1 + \frac{k_{red}[V_0^\infty] + k_{ox}[O_0^s]}{j\omega + 4\sqrt{k_{ads}k_{des}P_{O_2}N_0}} \right] = R_t + \frac{R_{ads}}{1 + j\omega R_{ads}C_{ads}} \quad [11]
\]

If the values of \(R_t\), \(R_{ads}\) and \(C_{ads}\) can be identified from the distribution, the model parameters \(k_{ads}\), \(k_{des}\), \(k_{red}\) and \(k_{ox}\) can be calculated, if the concentrations \([V_0^\infty]\), \([O_0^s]\) and \(N_0\) are known.

**RESULTS AND DISCUSSION**

\(R_t\) is the charge transfer resistance and is in inverse proportion to the electronation rates \(k_{ox}\) and \(k_{red}\). In the case of fast adsorption and desorption the reaction is controlled by charge transfer. In the opposite case, the reaction is controlled by the adsorption/desorption process. The impedance curve of \(Z_F\) is shown in fig. 6a. \(R_t\) is purely ohmic whereas the adsorption/desorption process shows capacitative behaviour. This effect is not electrical but caused by the electrode surface acting as a reservoir of adsorbed oxygen ready for charge transfer.

Polarization effects at the electrode/electrolyte interface lead to the build-up of a double layer capacitance \(C_{dl}\) which conceals the Faradaic impedance. Little is known about the magnitude and nature of \(C_{dl}\). Values ranging from 0.1 \(\mu\)F/cm\(^2\) to 1 mF/cm\(^2\) have been estimated (4). Generally, \(C_{dl}\) acts in parallel to \(Z_F\) (fig. 5b). Then, \(C_{dl}\) causes the occurrence of a second semi-circle in the impedance curve (fig. 6a). The peak representing the adsorption/desorption process in the distribution function at \(\tau_{ads} = R_{ads}C_{ads}\) and with the area \(R_{ads}\) is consequently split into two peaks with the joint area \(R_{ads} + R_t\) (fig. 6b).

The distribution function representing the oxygen reduction process has two peaks. From the peak parameters the kinetic rate constants can be estimated under the following assumptions: (1) the simple reaction model developed for the Pt,\(O_2(g)\)|YSZ system is also applicable to a LSM,\(O_2(g)\)|YSZ cathode. (2) \(N_0\), \([V_0^\infty]\) and \([O_0^s]\) are constant and known.

The general strategy for the identification of rate constants is to simulate cell parameter
Figure 7: Relaxation distributions from (a) impedance measurement data and (b) simulated from the physical sub-model (values for \( N_0 \), \([V_0] \), \([O_0] \) from (4), \( C_{dl} = 1 \mu F/cm^2 \)), both for variation of \( pO_2 \) at the cathode.

variations according to the physical sub-model and to compare the resulting distribution functions to a series of impedance measurements in which the same cell parameter was varied. Fig. 7 shows series of simulations and measurements for variation of \( pO_2 \) at the cathode. Peak A exhibits a \( pO_2 \)-dependence which is qualitatively similar to the simulation as shown in fig. 8. Because no sufficient information on the values of \([V_0] \), \([O_0] \), and \( N_0 \) was at present available, the rate constants could not be directly identified. However, in accordance with earlier results peak A can be ascribed to the oxygen reduction (6).

Figure 8: Qualitative comparison of peak parameters from measurement and simulation: (a) Frequency of peak A (fig. 7) representing oxygen reduction and (b) area under peak. The parameters from simulation are normalized to the highest value of the peak parameters from measurement.
The method described above is applicable to further reaction mechanisms in SOFC and other electrochemical systems when an impedance representation of the respective processes is available.

CONCLUSIONS

A numerical "relaxation times" method for the evaluation of impedance spectra was presented. The method allows to calculate the distribution of the dynamic constants of polarization processes directly from the data, without the use of equivalent circuit models and non-linear curve fit. The resolution of polarization processes is about six times higher than with curve fit.

From the peak parameters of the distribution function a mathematical model of the impedance in state space form is built into which impedance representations of physical sub-models can be inserted. A general strategy for the identification of kinetic rate constants from distribution functions was presented.

The relaxation times method is currently being implemented into a software tool in order to make the method available to other groups. Information on the status of the project is available from (10).

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