IDENTIFICATION OF POLARIZATION PROCESSES
IN SOFC ELECTRODES

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ABSTRACT

For the optimization of SOFC single cells it is important to understand the physical nature of polarization processes occurring in SOFC electrodes during operation. Information about these processes was gathered by measuring the electrochemical impedance of the cell. Series of impedance measurements were carried out in which one parameter of cell operation was varied. Distributions of relaxation frequencies of polarization processes were calculated directly from the impedance spectra by a newly developed method without the need for an equivalent circuit model. Processes are represented by peaks in the distribution function. By studying the influence of cell parameters on the distribution function, assumptions about the physical nature of the underlying processes can be made. Some examples of parameter variations are given in this study: oxygen partial pressure at the cathode and current load. Distributions of impedance spectra measured before and after initial current loading of the cell were examined.

INTRODUCTION

For the development of a physico-chemical model of SOFC single cells it is necessary to understand the various polarization processes and their dependence on operational and material parameters. The dominating polarization processes have to be determined in order to further optimize the cell with respect to efficiency and long term stability. Electrochemical impedance spectroscopy (EIS) is used for investigating possible polarization processes. The obtained impedance spectra are commonly evaluated by approximation to a model function represented by an equivalent circuit (1). This approach has some disadvantages because a priori knowledge of the physical processes in the cell is needed and the equivalent circuit is ambiguous (2). In this work an alternative method for analyzing impedance spectra is used which yields a distribution function \( g(f) \) of polarization processes directly from the impedance spectrum (3, 4). No equivalent circuit has to be assumed. Each process is represented by a peak in the distribution function. The peak is characterized by its relaxation frequency, the polarization resistance and the characteristic shape of the peak, bearing information about the underlying loss or degradation mechanism.

EXPERIMENTAL

The investigated single cells consisted of a 150\,\mu m thick 8YSZ electrolyte (8YSZ: zirco-
nia doped with 8 mol% yttria) with a La$_{0.75}$Sr$_{0.2}$MnO$_3$ (LSM) cathode and a Nickel/8YSZ cermet anode (75 mol% Ni). After screen printing of the electrodes the cells were sintered for 5 hours at 1300 °C in air (5). The electrodes had an area of 10 cm$^2$ and were contacted with Pt and Ni mesh, respectively. The cathode was supplied with 500 sccm N$_2$/O$_2$ mixture and the anode was fed with hydrogen which could be humidified between 0 and 90% (6). The impedance measurements were carried out with a SOLARTRON 1260 frequency response analyzer within a frequency range from 100 mHz to 1 MHz. To investigate the parameter dependence of the processes, series of impedance measurements were carried out in which one cell parameter was varied (oxygen partial pressure, hydrogen partial pressure, fuel utilization, temperature, current load etc.). Distributions functions of polarization processes were calculated directly from impedance data using the method described in (4). The contribution of each process to the total polarization resistance $R_{pol}$ was obtained by non-linear fit of the distribution curves to a set of model peaks. The error in the computation of the distribution function $g(f)$ due to the limited frequency range was reduced by extrapolation of the measured data (4). As the evaluation of impedance spectra by this new method is just at the beginning only a limited number of measured impedance spectra will be shown.

**RESULTS AND DISCUSSION**

Fig. 1a shows a typical impedance spectrum of a SOFC single cell. At first glance there are two arcs in the complex plane which can be assigned to two polarization pro-

![Figure 1:](image)

**Figure 1:** a) Typical impedance spectra of a SOFC single cell and b) corresponding distribution function. Unlike the nyquist plot, at least 6 polarization processes are visible in the distribution curve.
cesses. However, the computation of the distribution function \( g(f) \) of relaxation frequencies (Fig. 1b) indicates that there are at least six processes each represented by a single peak. This result implies that the frequency resolution of the method is higher than that of the conventional curve fit with an equivalent circuit. The area under each peak corresponds to the polarization resistance \( R_{pol,i} \) of the respective process and was calculated by non-linear fit of \( g(f) \) with six Gauss peaks.

Influence of Oxygen Partial Pressure

Impedance series were carried out at various temperatures (850, 900 and 950 °C) with increasing \( p_{O_2,C} \) at the cathode (from air to pure oxygen). One set of measurements was made at open circuit conditions (OCC) and another set at a current load of \( j = 0.3 \text{ A/cm}^2 \). As an example, a series of distribution curves at \( T = 950 \) °C and \( j = 0.3 \text{ A/cm}^2 \) is shown in Fig. 2. The following discussions will focus on the two processes A and B with a relaxation frequency of approximately \( f_A \approx 2 \text{ Hz} \) and \( f_B \approx 2 \text{ kHz} \). They depend on \( p_{O_2,C} \) as they increase with decreasing \( p_{O_2,C} \). The polarization resistances of these two processes were determined by nonlinear peak fit and are plotted in Fig. 3a and Fig. 4, respectively. In addition, a \( \log R_{pol} - \log p_{O_2} \) plot is given in Fig. 3b. The following law is assumed for process A:

\[
R_{pol,A} \propto p_{O_2,C}^x
\]  

[1]

Under OCC the exponent in Eq. [1] was calculated from the slope in the double-logarithmic plot as \( x = -0.4 \). However, under electric load two different slopes are apparent in Fig. 3b.

Figure 2: Series of distribution curves at different \( p_{O_2,C} \) at the cathode (\( T = 950 \) °C, \( j = 0.3 \text{ A/cm}^2 \)). Two processes A and B with dependence on \( p_{O_2,C} \) are observed.
Figure 3: a) $R_{pol,A}$ ($f_A \approx 2$ Hz) as a function of $pO_2,c$ and $T$ at OCC (solid symbols) and under current load (open symbols). The double-logarithmic plot in b) indicates that a second process appears under current load.

In the range of 1 - 0.4 atm, $x$ was calculated as $-0.3$ and which then changes to $-0.6$ for $pO_2,c < 0.4$ atm. This implies that a second polarization process with a relaxation frequency close to $f_A$ occurs under current load. This assumption is supported by the fact that in the distribution function $g(f)$ the width of peak A increases and its relaxation frequency shifts to lower frequencies. At present, the two processes are too close to be separated by the method. Furthermore a change in the temperature dependence is visible, although the temperature dependence of process A is weak under both conditions (an activation energy of $E_A = -60$ meV at OCC and $E_A = 130$ meV under current load was calculated). The physical nature of process B is different from process A because its dependence on $pO_2,c$ strengthens with falling temperature and this dependence is more distinct under current load. A similar law like Eq. [1] was assumed for $R_{pol,B}$ and the calculated exponents $x$ are given in Table I. The activation energy was determined as $E_A = 1.1$ eV and $E_A = 1.5$ eV at OCC and under current load, respectively. This implies that process B becomes the dominating process at lower temperatures in comparison to process A.

Figure 4: $R_{pol,A}$ ($f_A \approx 2$ Hz) as a function of $pO_2,c$ and $T$ at OCC (left) and under current load (right)
| $T/ ^\circ C$ | OCC | $j = 0.3$ A/cm$^2$ |
|------------|-----|------------------|
| 950        | -0.2| -0.1             |
| 900        | -0.2| -0.4             |
| 850        | -0.2| -0.4             |

Table 1: Exponent $x$ of Eq. [1] for process B. The dependence of $R_{\text{pol,B}}$ on $p_{O_2,C}$ increases under current load as the temperature decreases.

**Influence of Current Load**

To determine the influence of current load on the polarization processes impedance spectra at various current densities ranging from 0 to 0.7 A/cm$^2$ were measured. Oxygen and air were used as oxidant, respectively. The corresponding distributions are shown in Fig. 5 and Fig. 6. Again a dominant process at $f_A \approx 2$ Hz is observed. $R_{\text{pol,A}}$ steadily decreases in oxygen operation as the current density increases. When air is used as oxidant $R_{\text{pol,A}}$ firstly decreases and then increases for current densities larger than 0.3 A/cm$^2$. In addition the peak broadens and the relaxation frequency shifts slightly towards lower frequencies. A second peak becomes apparent. This result was compared with I/V characteristics. The voltage losses shown in Fig. 7 were measured with reference electrodes. The slope of the curves corresponds to the polarization resistance of the cathode. The two characteristics are similar for small current densities. For current densities larger than 0.3 A/cm$^2$ the losses in air operation exceed those in oxygen. This is in agreement with the results from distribution functions since a larger slope of the cathode losses means an increased polarization resistance.

**Influence of Changes in the Microstructure**

During the initial load of the single cell with electrical current the microstructure of

Figure 5: Distribution curves as a function of current density with oxygen as oxidant ($T = 950 \, ^\circ C$). $R_{\text{pol,A}}$ decreases steadily with increasing current density.
Figure 6: Distribution curves at increasing current density with air as oxidant ($T = 950 \, ^\circ\text{C}$). A second peak appears at current densities larger than 0.3 A/cm$^2$.

Figure 7: Voltage losses at the cathode measured with reference electrodes obtained from $I/V$ characteristics. As the current density exceeds 0.3 A/cm$^2$ the voltage losses in air are larger than those in oxygen.

anode and cathode changes. Especially the cathode/electrolyte interface improves because poor conducting secondary phases of $\text{La}_{2}\text{Zr}_{2}\text{O}_{7}$ disappear (7). Fig. 8 shows the influence of this "activation" onto the polarization processes. The polarization resistances of the two dominating relaxation processes at $f \approx 2 \, \text{Hz}$ and $f \approx 30 \, \text{Hz}$ decrease drastically. Refering to the previous results one can conclude that the process at 2 Hz can be assigned to the interface cathode/electrolyte.
**CONCLUSIONS**

The investigations showed that the calculation of distribution functions of relaxation frequencies is a useful method for analyzing impedance spectra. The frequency resolution of this method is higher than that of the conventional curve fit with an equivalent circuit, i.e. more information about the polarization processes can be gained from the same data. Polarization processes are characterized by their relaxation frequency and their polarization resistance. Thus a direct correlation between cell parameters and the polarization resistance of an individual polarization process can be made. Impedance series with variation of $p_{O_2, c}$, current density and temperature were evaluated for the first time by the new method. In future, impedance series with different parameters variations will be evaluated.

**REFERENCES**

1. B. A. Boukamp, *Solid State Ionics*, 20, 31 (1986).
2. J. R. Macdonald, *Impedance spectroscopy*, p. 95, Wiley Interscience, New York (1987).
3. A. D. Franklin and H. J. deBruin, *Phys. stat. sol.(a)*, 75, 647 (1983).
4. H. Schichlein, M. Feuerstein, A. Müller, A. Weber, A. Krügel and E. Ivers-Tiffée, *These proceedings*.
5. E. Ivers-Tiffée, W. Wersing and H. Greiner, in *Electroceramics IV: Electroceramics and Applications I-III*, R. Waser, Editor, p. 719, Augustinus Buchhandlung (1994).
6. A. Müller, A. Weber, H.-J. Beie, A. Krügel, D. Gerthsen and E. Ivers-Tiffée, in *Proceedings of the 3rd European Solid Oxide Fuel Cell Forum*, P. Stevens, Editor, European Fuel Cell Forum, 353 (1998).
7. A. Weber, R. Männer, R. Waser and E. Ivers-Tiffée, *Denki Kakagu*, 64, 582 (1996).