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A Method to Separate Process Contributions in Impedance Spectra by Variation of Test Conditions

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Many processes contribute to the overall impedance of an electrochemical cell, and these may be difficult to separate in the impedance spectrum. Here, we present an investigation of a solid oxide fuel cell based on differences in impedance spectra due to a change of operating parameters and present the result as the derivative of the impedance with respect to \( \ln(f) \). The method is used to separate the anode and cathode contributions and to identify various types of processes.

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Mathematical techniques have been proposed to assist in the problem of identifying electrochemical processes in impedance spectra. Schichlein et al.\(^1\) have presented a technique using Fourier transformation of experimental impedance spectra in order to determine the distribution function in the time domain. In a series of papers Vladikova, Stoynov, and co-workers\(^2\) use the derivative of the impedance with respect to frequency as a working variable. They resolve the impedance spectra into a series resistance, a polarization resistance, and a polarization capacitance, all of which are frequency dependent. A somewhat similar approach was later presented by Darowicki.\(^4\)

These methods extract information about the contributing processes from a single impedance spectrum. In contrast, we use several spectra to isolate the process contributions prior to the data treatment. This enables us to identify and study the contributing processes separately.

The cathode and anode electrode arcs typically overlap in impedance spectra recorded on solid oxide fuel cells (SOFCs). To overcome this problem, impedance spectroscopy has been applied to both symmetrical cells (cells with two identical electrodes on either side of the electrolyte) and to electrodes in a three-electrode setup.\(^3\)\(^-\)\(^9\) Both experimental arrangements suffer the drawback of differing substantially from commercial cells due to the differences in manufacturing. Not only the interpretation of the spectra but also the performance and stability of the electrodes differ from that of anode-supported SOFCs with a thin (10 \( \mu m \)) electrolyte. In this work, an SOFC is investigated and, using the presented method, six electrode processes are resolved in the impedance spectra.

The method is based on the change that occurs in an impedance spectrum when an optional operation parameter such as partial pressure of a reactant, temperature, etc., is changed. An impedance spectrum is recorded just before such a change and another spectrum just after the change. The real part of the spectra is differentiated with respect to \( \ln(f) \), where \( f \) is the frequency. The difference in this quantity, \( \Delta Z'(f) \), between the two spectra is named \( \Delta Z' \) and is plotted vs \( \ln(f) \). The resulting spectrum enables detection of processes affected by the altered operation parameter. The difference in the imaginary part of the two impedance spectra (named \( \Delta Z'' \)) contains almost the same information. However, plotting \( \Delta Z' \) vs \( \ln(f) \) does not provide the same resolution in the frequency domain. This is discussed theoretically in the appendix and confirmed by the presented experiments. In addition, the \( \Delta Z' \) spectrum may provide detailed information about the nature of the involved processes.

Experimental

The tested cell is an anode-supported thin electrolyte SOFC.\(^11\),\(^12\)

It has a porous support layer of Ni and yttria-stabilized zirconia (YSZ) with a thickness of 300 \( \mu m \). The hydrogen/steam electrode (thickness 10 \( \mu m \)) is porous and made of Ni and YSZ. The dense YSZ electrolyte has a thickness of 10 \( \mu m \). The air/O\(_2\) electrode is porous and 20 \( \mu m \) thick. It is made of strontium-doped lanthanum manganite (LSM) and YSZ.

The cells were tested at ambient pressure in alumina housing between two gas-distributor plates made of Ni and LSM. Ni and Au foils contacting the Ni and LSM gas distribution layers, respectively, were used for current collection. Further details on the setup are given elsewhere.\(^13\)

The cell was tested at 750°C at open-circuit voltage (OCV). The feed gas to the LSM/YSZ electrode was O\(_2\)/N\(_2\) mixtures at a rate of 20 L/h ranging from pure O\(_2\) to 25 vol % O\(_2\). The feed gas to the Ni/YSZ electrode was H\(_2\)/H\(_2\)O mixtures at a rate of 25 L/h ranging from 5 vol % H\(_2\)O and 50 vol % H\(_2\). In one experiment the feed gas to the Ni/YSZ was different; the electrode was fed with a D\(_2\)/D\(_2\)O (or H\(_2\)/H\(_2\)O) mixture at a rate of 10 L/h. The D\(_2\)O (or H\(_2\)O) concentration was 20 vol %. In this experiment the isotope was exchanged but the humidity and flow rate was kept constant. A Solartron 1260 was used for the impedance measurements. All spectra were recorded with six measurement points per decade.

Theory

The performance of electrochemical cells depends on a sequence of processes, such as mass transfer of reactants/products, charge-transfer reactions, electronic and ionic conduction, etc. The overall impedance can be represented as a series of impedance elements describing the individual processes, i.e.

\[
Z(\omega) = \sum_{i} z_i(\omega)
\]

(1)

The individual \( z_i \) elements may be parallel circuits themselves, consisting of several processes. However, parallel connections of impedance elements such as (\( RC \)) circuits, (\( RQ \)) circuits, and Gerischer elements are redundant and no separation into individual elements by means of electrochemical measurement techniques may be possible. Even when \( Z \) is known in a large frequency range, it may prove difficult if not impossible to determine the individual \( z_i \) elements.

Now suppose an operation parameter, \( \Psi \) (flow rate, gas composition, temperature, etc.), is slightly changed from condition A to condition B. As a result, a number of impedance elements, \( z_j \), are modified and a number, \( z_k \), stays constant. Hence, for this small change in \( \Psi \), say \( \Delta \Psi = \Psi_B - \Psi_A \), the change in \( Z \) can be written as

\[
\Delta Z(\omega) = \sum_{j \neq k} \Delta z_j(\omega) + \Delta z_k(\omega)
\]

(2)

The above method provides a systematic way of accounting for changes in the impedance spectrum due to changes in operating parameters. The \( \Delta z_j(\omega) \) and \( \Delta z_k(\omega) \) are then used to extract data on the individual processes.
The size of the impedance arc is changed, but the characteristic constant. At the frequency various increases from one or a few elements present in the sum of elements in Eq. 1. For the closed symbols. Each impedance arc are shown in the figure. Values of the circuit in conditions A and B. The values of the circuit elements for as a change in capacitance $C$. The $\Delta Z'$ spectrum $R$ increases and $C$ decreases. Two subtypes are defined. “Capacitive” is change in capacitance $C$ with a constant $R$. The $\Delta Z'$ spectra “C decreases” and “C increases” in Fig. 2 are capacitive. “Resistive” is change in the resistance $R$ with a constant $C$. The $\Delta Z'$ spectra “R increases” and “R decreases” in Fig. 2 are resistive.

A number of simple models of physical changes result in a time-invariant $\Delta Z'$ spectrum. For instance, a change in the exchange volume in a continuous stirred tank reactor (CSTR) model of conversion impedance would result in a time-invariant $\Delta Z'$ spectrum. Likewise, one could think of processes related to the triple-phase boundary (TPB) (such as adsorption or desorption) that would produce a time-invariant $\Delta Z'$ spectrum if the length of the active triple phase boundary is changed (because the double-layer capacitance is inverse proportional to the TPB length, whereas the resistance associated with the process is proportional to the TPB length).

In Fig. 2, the time-invariant $\Delta Z'$ spectrum only attains positive values or negative values, whereas both the capacitive and resistive $\Delta Z'$ spectra attain both negative and positive values. In the Appendix it is shown that this also applies to (RQ) circuits and to Gerischer elements. This makes it possible to distinguish the time-invariant $\Delta Z'$ spectrum from the capacitive or resistive $\Delta Z'$ spectrum. Note that for a time-invariant $\Delta Z'$ spectrum of an (RC) circuit, $\Delta Z'(\omega)$ has its peak frequency (i.e., local maximum or minimum) at $\omega^*$.

Results

Figure 3 shows impedance spectra recorded on an SOFC. The upper figure shows spectra recorded with $O_2$ diluted with 0, 20, 50, or 75 vol % $N_2$ supplied to the LSM/YSZ electrode at a rate of 20 L/h. The Ni/YSZ electrode was fed with $H_2$ containing 50 vol % $H_2O$ at a rate of 25 L/h. The lower figure shows spectra recorded with pure $O_2$ (50 vol % $N_2$) supplied at a rate of 20 L/h to the LSM/YSZ electrode and with $H_2$ containing 5, 20, or 50 vol % $H_2O$ supplied at a rate of 25 L/h to the Ni/YSZ electrode.

At first glance, the spectra in Fig. 3 show three separable arcs. In order to obtain more detailed information about the number of $z_i$'s that contribute to the SOFC spectra and to which of the electrodes the $z_i$'s belong, the spectra in Fig. 3 were used to form $\Delta z_i$ spectra.

Referring to the upper part of Fig. 3, an impedance spectrum was recorded with pure $O_2$ to the LSM/YSZ electrode. Then, the gas to the LSM/YSZ electrode was changed to $O_2$ diluted with $N_2$ and another spectrum was recorded. Finally, the gas was reverted to pure.
O₂ and a third spectrum was recorded. A ΔZ′ spectrum was made using the first and second impedance spectrum as described in the previous section. Another ΔZ′ spectrum was made using the second and third spectrum. By subtracting the second ΔZ′ spectrum from the first and dividing by two, an average ΔZ′ spectrum was made.

The average ΔZ′ spectrum is better than the single-shift ΔZ′ spectrum in the sense that the signal-to-noise ratio is increased by a factor of 2. Furthermore, time-dependent passivation or activation of the electrodes that is unaffected by the gas change is suppressed by an order of magnitude.

In order to assure that a drift or extended relaxation due to the gas change does not influence the impedance spectra, it should be checked that the spectra obey the Kramers–Kronig relations. Because electrical circuit models satisfy the Kramers–Kronig relations, a system can be judged to be stationary if a satisfactory fit to an equivalent circuit model can be obtained. 

All the impedance spectra are tested by modeling the spectra with an equivalent circuit of the Voigt type, LR(RQ)W₀(RQ)(RQ) ×(RQ). L is an inductance in series with R, an ohmic resistance. The brackets indicate that (RQ) is a parallel circuit consisting of a resistance and a constant phase element. W₀ is a finite-length Warburg element with a transmissive boundary condition. The error between fit and measurement relative to |Z| was less than 1% for both the real and imaginary part in all spectra at all frequencies. Hence, drift or extended relaxation is known to be limited.

The noise in the resulting average ΔZ′ spectrum was further reduced by using a moving average of three points, plotting each point, ΔZ′(ωₙ₋₁), as an average of the values obtained at ωₙ₋₁, ωₙ, and ωₙ₊₁. The result is shown in Fig. 4. A noise-reduced (or moving average of three points) ΔZ′ spectrum from 0 vol % N₂ to 0 vol % N₂ was made to measure the uncertainty or background noise of the measurement technique and is plotted as the bold black line.

The number of measurement points used in this work is six points per frequency decade. The synthetic ΔZ′ spectra (shown in the Appendix) indicate that the peaks, which we probably would find, are stretched over a frequency decade or even more. For this reason, it is unlikely to find any additional features in the ΔZ′ spectra by increasing the number of frequency points per decade.

If the number of points were increased, the time used to produce the impedance spectra would increase. This may increase possible errors due to drift, electrode relaxation, or unstable measurement conditions. Increasing the number of ac cycles at each measurement point also decreases the noise provided that no changes over time take place. Thus, the optimal number of points per frequency decade as well as the optimal number of ac cycles per point has to be assessed in each case.

The ΔZ′ spectra in Fig. 4 reveal three separable peaks, indicating that at least three different types of processes occur at the LSM/YSZ electrode and contribute to the impedance spectra. The summit frequency, fₚ = ωₚ/2π, of the LSM/YSZ electrode arcs in pure O₂ can be approximated by drawing a straight line through the peaks of the ΔZ′ spectrum to the x axis. The frequency at the intercept with the x axis is the approximate summit frequency for the LSM/YSZ electrode arcs in pure O₂. These frequencies are (<10 Hz; ~300 Hz; ~10 kHz). The processes behind the three observed peaks are elaborated on in the next section.

Referring to the lower part of Fig. 3, an impedance spectrum was recorded with H₂ containing 50 vol % H₂O and another impedance spectrum was recorded. Finally, the steam concentration was subsequently changed to 5 or 20 vol % H₂O and another impedance spectrum was recorded. The steam concentration was reverted back to 50 vol % H₂O and another impedance spectrum was recorded. The spectra were used to produce average noise-reduced ΔZ′ spectra like the ones shown in Fig. 4. The result is shown in Fig. 5. A noise-reduced ΔZ′ spectrum from 50 vol % H₂O to 50 vol % H₂O was made to determine the background noise of the measurement technique and is plotted as the bold black line.

The ΔZ′ spectra in Fig. 5 reveals three separable peaks, indicating that at least three different types of processes occur at the Ni/YSZ electrode and contribute to the impedance spectra. Again, the summit frequency can be found by drawing a straight line through the ΔZ′ spectra peaks to the x axis. The frequency at the intercept with the x axis is the approximate summit frequency for the electrode arcs in H₂ containing 50 vol % H₂O. The frequencies are (<10 Hz; ~300 Hz; ~2 kHz).

The gas-diffusion peak is not clearly visible in Fig. 5. To enhance the visibility of the gas-diffusion process, a H—D isotope experiment was made. First, a H₂ impedance spectrum (H₂ containing 20% H₂O at a rate of 10 L/h) was recorded and subsequently a D₂
noise-reduced uncertainty measure of the setup. The summit frequencies were reported as 0.1–10 Hz for the total pressure. These frequencies in good agreement with the low-, medium-, and high-frequency peaks in Fig. 4. The arc with a summit frequency of 300 Hz to dissociative adsorption/ desorption, the characteristic frequency for the impedance element $\omega_p$. This is confirmed experimentally in Fig. 6, where the $\Delta Z''$ spectrum reveals the gas-diffusion peak in contrast to the $\Delta Z'$ spectrum. The presented method to analyze differences in impedance spectra by variation of test conditions may be applied to other electrochemical devices, because it enables a selective study of process contributions to the impedance.

**Conclusion**

An SOFC was investigated based on differences in impedance spectra due to a change of operating parameters. Plotting the difference in the derivative with respect to $\ln(f)$ of the real part of the impedance is shown to be helpful in separating processes that overlap in impedance spectra. The produced $\Delta Z'$ spectra revealed three identifiable peaks at the LSM/YSZ electrode and three at the Ni/YSZ electrode. Each peak in the $\Delta Z'$ spectra corresponds to a change in a process that contributes to the impedance spectra.

The three $\Delta Z'$ spectrum peaks observed at the LSM/YSZ electrode had peak frequencies around ($10 \text{ Hz}$, $300 \text{ Hz}$, $10 \text{ kHz}$) at 750°C. This is in good agreement with previous findings in a three-electrode-setup and a symmetrical-cell setup. The Ni/YSZ electrode has previously been investigated in a three-electrode setup where a gas-conversion arc ($0.1$–$1 \text{ Hz}$), a gas-diffusion arc ($10 \text{ Hz}$–$1 \text{ kHz}$), and a gas-solid or solid-solid arc ($1$–$10 \text{ kHz}$) were found. This is in good correspondence with the observed $\Delta Z'$ spectrum peaks, which had peak frequencies at ($<10 \text{ Hz}$, $30 \text{ Hz}$, $2 \text{ kHz}$).

Evidence for gas diffusion at the Ni/YSZ electrode was revealed in an isotope experiment where hydrogen was exchanged with deuterium. The produced $\Delta Z'$ spectrum peaks reveal a peak around $80 \text{ Hz}$. For simplicity, the high-frequency peak is referred to as a gas-solid reaction.
Appendix

Below we calculate \( Z \) and \( \dot{Z} \) for an (RC) circuit, an (RQ) circuit, and a Gerischer element. After this, some discussion on \( \Delta Z' \) follows, and finally an example of a \( \Delta Z' \) spectrum is given.

\((RC)\) circuit

The impedance, \( Z(u) \), for an (RC) circuit where \( u = 2\pi f \) is the angular frequency is given as

\[
Z(u) = \frac{R}{1 + juRC} = \frac{R}{1 + xu} = \frac{R}{1 + x} \quad [A-1]
\]

where \( u^* = 1/RC \) and \( x = juu^* \). We can now find the derivative with respect to \( \ln(u) \) as

\[
\dot{Z} = \frac{dZ}{d\ln(u)} = -\frac{R}{(1 + xu)^2} \quad [A-2]
\]

\((RQ)\) circuit

The impedance, \( Z(u) \), of an (RQ) circuit, where \( Q \) is a constant-phase element with the impedance \( Z_Q(u) = 1/(ju\tau)^\nu \), is given as

\[
Z(u) = \frac{R}{1 + RE(j\tau)^\nu} = \frac{R}{1 + y} \quad [A-3]
\]

where \( u^* = (RE)^{-\nu} \) and \( y = (ju\tau)^\nu \). The derivative with respect to \( \ln(u) \) can be found as

\[
\dot{Z} = \frac{dZ}{d\ln(u)} = -\frac{R}{(1 + y)^2} \left[ \frac{y}{u\tau} \right]^\nu \frac{1}{(1 + y)^2} \quad [A-4]
\]

Note that when \( n = 1 \), Eq. A-3 reduces to A-1 and A-4 reduces to A-2.

\(\text{Gerischer element}\)

The impedance for a Gerischer element may be written as

\[
Z(u) = \frac{R}{\left(1 + auu^*\right)^\nu} = \frac{R}{\left(1 + xu\right)^\nu} \quad [A-5]
\]

and the derivative with respect to \( \ln(u) \) is found as

\[
\dot{Z} = \frac{dZ}{d\ln(u)} = -\frac{R}{\left(1 + auu^*\right)^2} \frac{1}{a} \frac{au}{\left(1 + auu^*\right)} \quad [A-6]
\]

For the (RC) element, separating into real and imaginary parts yields

\[
Z = \frac{R}{1 + auu^*} - juRauu^* \quad [A-7]
\]

and

\[
\dot{Z} = \frac{2R(uuu^*)^2}{\left[1 + (uu)^2\right]^2} + j\frac{R(u^2uu^*)}{\left[1 + (uu)^2\right]^2} \quad [A-8]
\]

From Eq. A-7 and A-8 it is seen that

\[
\Delta Z' = -\frac{Z'}{R} \quad [A-9]
\]

where \( \Delta Z' \) is the real part of \( Z' \) and \( Z' \) is the imaginary part of \( Z \). This explains why \( Z' \) produces a sharper and more well-defined peak than \( Z' \). From Eq. A-9 it is also seen that \( Z' \) and \( Z' \) has a maximum (or minimum) at the same frequency. Taking the derivative of Eq. A-7 with respect to \( u^* \), this frequency can be shown to be \( u^* \). Figure A-1 shows a plot of \( Z' \) and \( Z' \) for an (RQ), and the Gerischer and (RC), elements, given the values in Table A-I, condition A.

In general, an impedance spectrum is a sum of responses from several processes with different characteristic time constants. For simplicity, let us examine the response arising from two (RC)s in series, which we shall denote (RC)\(_1\) and (RC)\(_2\).

For such a circuit we can find

\[
Z' = -\frac{2R(uu)u^2}{\left[1 + (uu)^2\right]^2} \quad [A-10]
\]

where \( u^* = 1/RC \) for (RC)\(_1\) and \( u^* = 1/RC \) for (RC)\(_2\). If \( u^* \neq u^*_0 \), a \( Z' \) vs \( \ln(u) \) graph produces two overlapping peaks. We can also find

\[
Z' = -\frac{2R(uu)u^2}{\left[1 + (uu)^2\right]^2} \quad [A-11]
\]

which also gives two peaks in a Bode plot, but the peaks are not as well separated as for \( Z' \). Taking the square of Eq. A-11 does not result in well-separated peaks in a Bode plot due to the formation of a cross term of the form

\[
\frac{u^*}{1 + (uu)^2} \quad [A-12]
\]

Now assume that an operation parameter \( \nu \) is changed from condition A to B such that (RC)\(_1\) is affected but (RC)\(_2\) remains constant. It then follows that \( \Delta Z' \) is given as

\[
\Delta Z' = \frac{2R(uu)u^2}{\left[1 + (uu)^2\right]^2} \quad [A-13]
\]

If \( u^*_0 = u^*_0 \), Eq. A-13 can be further simplified to give

\[
\Delta Z' = 2\frac{R^2}{R^2} \quad [A-14]
\]

Comparing the real part of Eq. A-8 and A-14, it is seen that \( \Delta Z' \) produces a peak with similar shape to the \( \Delta Z' \) peak shown in Fig. A-1 with center at \( u^*_0 \), but rescaled with a factor \( R^2/R^2 \). Given the same assumptions as for the calculation of \( \Delta Z' \), \( \Delta Z' \) can be found as

![Figure A-1. \( Z' \) and \( Z' \) for \((RQ)\), a Gerischer, and an \((RC)\), with the values specified in Table I, condition A. Note that \( Z' \) produces sharper and more well-defined peaks than \( Z' \).](image-url)
thin lines are $\Delta Z'$ and $\Delta Z''$ for the impedance of (RQ)_1, Gerischer$_2$, and (RC)$_3$ in series at condition A and B. The inset is a plot of $\Delta Z'$ and $\Delta Z''$ from a single impedance element in series at condition A and B.

![Figure A-2. $\Delta Z'$ and $\Delta Z''$ for (RQ)$_1$, Gerischer$_2$, and (RC)$_3$ in series, undergoing a change in $\Psi$ from condition A to B as specified in Table A-I. The thin lines are $\Delta Z'$ and $\Delta Z''$ for the individual elements. The inset is a plot of $\Delta Z'$ and $\Delta Z''$ from a single impedance element in series at condition A and B.](image)

$\Delta Z' = \frac{(R_{A'} - R_{B'})\omega/\omega^*}{1 + (\omega/\omega^*)^2}$  \[A-15\]

which produces a peak with a similar shape to the $Z'$ peak shown in Fig. A-1 with center at $\omega^*$, but rescaled with a factor $(R_{A'} - R_{B'})/R_{A'}$. Looking at Eq. A-3 through A-6, it is clear that if $\omega^*$ is preserved, the peak shape is preserved. From Fig. A-1 it is then seen that a time-invariant (i.e., $\omega^*$-preserving) $\Delta Z'$ spectrum (from a single impedance element) only attains positive or negative values (and not both positive and negative values.)

Figure A-2 presents $\Delta Z'$ and $\Delta Z''$ for an (RQ), a Gerischer, and an (RC) element in series, undergoing a change in $\Psi$ from condition A to B. The elements are referred to as (RQ)$_1$, Gerischer$_2$, and (RC)$_3$, and the parameter values for the elements are specified in Table A-I. (RQ)$_1$ undergoes a time-invariant change, Gerischer$_2$ undergoes a resistive change, and (RC)$_3$ undergoes a capacitive change. Note that the three peaks are better resolved in the $\Delta Z'$ spectrum than in the $\Delta Z''$ spectrum.

References