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

Søren Højgaard Jensen,a,z Anne Hauch,a,b Peter Vang Hendriksen,a Mogens Mogensen,a,* Nikolaos Bonanos,a and Torben Jacobsen,b  

aFuel Cells and Solid State Chemistry Department, Risø National Laboratory, and bDepartment of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark  

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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Experimental  

The tested cell is an anode-supported thin electrolyte SOFC. It has a porous support layer of Ni and yttria-stabilized zirconia (YSZ) with a thickness of 300 μm. The hydrogen/steam electrode (thickness 10 μm) is porous and made of Ni and YSZ. The dense YSZ electrolyte has a thickness of 10 μm. The air/O2 electrode is porous and 20 μm 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 O2/N2 mixtures at a rate of 20 L/h ranging from pure O2 to 25 vol % O2. The feed gas to the Ni/YSZ electrode was H2/H2O mixtures at a rate of 25 L/h ranging from 5 vol % H2O and 50 vol % H2O to 20 vol % H2O.  

In one experiment the feed gas to the Ni/YSZ was different; the electrode was fed with a D2/D2O (or H2/H2O) mixture at a rate of 10 L/h. The D2O (or H2O) 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, \( z_i \), are modified and a number, \( z_j \), stays constant. Hence, for this small change in \( \Psi \), say \( \Delta\Psi = \Psi_B - \Psi_A \), the change in \( Z \) can be written as...
The size of the impedance arc is changed, but the characteristic constant.

Hence, with a careful choice of $\omega$, see the Appendix. Figure 1 shows the impedance arc of an circuit in conditions A and B. The values of the circuit elements for one or a few elements present in the sum of elements in Eq. 1.

Element values are given in the figure. Angular frequencies are presented for part of Eq. 4 can be rewritten as

$$\Delta Z = \frac{\partial Z(\omega)}{\partial \ln(\omega)} |_{B} - \frac{\partial Z(\omega)}{\partial \ln(\omega)} |_{A} \approx \sum_{j} (z_{j|B} - z_{j|A})$$

where $z'_{j}(\omega)$ is only known for a discrete set of frequencies \(\{\omega_{1}, \omega_{2} \ldots \omega_{nm}\}\), for the $n$th frequency between $2$ and $N - 1$, the real part of Eq. 4 can be rewritten as

$$\Delta Z'(\omega) \approx \frac{[Z'_{n}(\omega_{n+1}) - Z'_{n}(\omega_{n})]}{\ln(\omega_{n+1}/\text{rad s}^{-1}) - \ln(\omega_{n}/\text{rad s}^{-1})}$$

where $Z'_{n}(\omega)$ is the real part of the spectrum in Fig. 1 in condition A at the frequency $\omega$ and $Z'_{n}(\omega)$ is the real part of the other spectrum at $\omega$. $\Delta Z'(\omega)$ is plotted vs log frequency in Fig. 2 and labeled “$R_{2}$ inc., $C_{2}$ dec.” Such a plot of $\Delta Z'(\omega)$ vs log frequency is referred to as a $\Delta Z'$ spectrum. In Fig. 2, some other $\Delta Z'$ spectra are shown for various increases (all 10% increase) and decreases (all 9% decrease) of $R$ and $C$.

Two main types of $\Delta Z'$ spectra are defined: (i) Time invariant: The size of the impedance arc is changed, but the characteristic frequency $\omega_0$ is constant. The $\Delta Z'$ spectra “$R$ inc., $C$ dec.” and “$R$ dec., $C$ inc.” in Fig. 2 are time invariant because $\omega_0 = 1/RC$ is constant. (ii) Time variant: $\omega_0$ is changed. The size of the arc may be constant or change. 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 $\omega_0$.

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$_2$O at a rate of 10 L/h. The lower figure spectra recorded with pure O$_2$ (50 vol % N$_2$) supplied at a rate of 50 L/h to the δ/YSZ electrode and with H$_2$ containing 5, 20, or 50 vol % H$_2$O 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 $\delta$ that contribute to the SOFC spectra and to which of the electrodes the $\delta$ belong, the spectra in Fig. 3 were used to form $\Delta Z'$ 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 $\Delta Z'$ spectrum was made using the first and second impedance spectrum as described in the previous section. Another $\Delta Z'$ spectrum was made using the second and third spectrum. By subtracting the second $\Delta Z'$ spectrum from the first and dividing by two, an average $\Delta Z'$ spectrum was made.

The average $\Delta Z'$ spectrum is better than the single-shift $\Delta Z'$ 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.14,15

All the impedance spectra are tested by modeling the spectra with an equivalent circuit of the Voigt type. $LR(Q)W_W(Q)(RQ) \times (RQ)$. 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. $W_W$ is a finite-length Warburg element with a transmissive boundary condition.16 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 $\Delta Z'$ spectrum was further reduced by using a moving average of three points, plotting each point, $\Delta Z'(\omega_{n2})$, as an average of the values obtained at $\omega_{n1}, \omega_{n},$ and $\omega_{n+1}$. The result is shown in Fig. 4. A noise-reduced (or moving average of three points) $\Delta Z'$ 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 $\Delta Z'$ 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 $\Delta Z'$ 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 $\Delta Z'$ 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, $f_0 = \omega_0/2\pi$, of the LSM/YSZ electrode arcs in pure O2 can be approximated by drawing a straight line through the peaks of the $\Delta Z'$ 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 $\approx 10$ Hz; $\approx 300$ Hz; $\approx 10$ 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 to the Ni/YSZ electrode. The steam concentration was subsequently changed to 5 or 20 vol % H2O and another impedance spectrum was recorded. Finally, the impedance 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 electrode arcs in pure O2. The processes behind the three observed peaks are elaborated on in the next section.

The $\Delta Z'$ 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 $\Delta Z'$ 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 $\approx 10$ Hz; $\approx 300$ Hz; $\approx 2$ 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 with the two H₂ spectra.

When instead suggested that the observed low-frequency peak is due to gas
conversion in the gas-distributor plate on top of the electrode. When
a change in the active surface area would result in a time-invariant
peak. From classical statistical mechanics it is predicted that the
conductivity of D⁺ in a solid is 1/2 that of H⁺ because the “ambient
frequency” scales with 1/m, where m is the mass of the isotope. At 500 K the ratio between the H⁺ and D⁺ conductivity, σ_D/σ_H, in a
number of proton conductors has been observed to vary from 1.5 to
3.5.18 H₂ and D₂ diffusion in single-crystal Ni between 400 and
950°C has been investigated by Katz et al.19 The diffusion coefficient
was found to decrease about 20% at 750°C when shifting from
H₂ to D₂. Hence, a substitution of H₂ with D₂ is likely to cause a
decrease in the active surface area (the extension of the TPB) of the
electrode, which would cause the observed gas-solid ΔZ' spectrum
peak for the Ni/YSZ electrode reaction.

As discussed in the Appendix, the ΔZ' spectrum provides a bet-
ter resolution of the individual process contributions than a ΔZ‘
spectrum because it yields sharper and better-defined peaks around
ω*, the characteristic frequency for the impedance element ž. This is
confirmed experimentally in Fig. 6, where the ΔZ’ spectrum reveals
the gas-diffusion peak in contrast to the ΔZ‘ spectrum.

The presented method to analyze differences in impedance spec-
tra by variation of test conditions may be applied to other electro-
chemical devices, because it enables a selective study of process
contributions to the impedance.

Conclusion

An SOFC was investigated based on differences in impedance spec-
tra due to a change of operating parameters. Plotting the differ-
ence in the derivative with respect to ln(f) of the real part of the
impedance is shown to be helpful in separating processes that over-
lap in impedance spectra. The produced ΔZ’ spectra revealed three
identifiable peaks at the LSM/YSZ electrode and three at the Ni/
YSZ electrode. Each peak in the ΔZ’ spectra corresponds to a
change in a process that contributes to the impedance spectra.

The three ΔZ’ spectrum peaks observed at the LSM/YSZ electrode
had peak frequencies around [10 Hz, ~ 300 Hz, ~ 10 kHz] at
750°C. This is in good agreement with previous findings in a
three-electrode setup and a symmetrical-cell setup.6,6

The Ni/YSZ electrode has previously been investigated in a
three-electrode setup where a gas-conversion arc,1,4 (0.1–1 Hz),
a gas-diffusion arc6 (10 Hz–1 kHz), and a gas-solid or solid-solid arc1,10 (1–10 kHz) were found. This is in good correspondence
with the observed ΔZ’ spectrum peaks, which had peak frequencies
at [<10 Hz; ~ 80 Hz; ~ 2 kHz].

Evidence for gas diffusion at the Ni/YSZ electrode was revealed
in an isotope experiment where hydrogen was exchanged with deu-
terium. The produced ΔZ’ spectrum reveals a peak around 80 Hz.

Note that the gas-diffusion peak is only
revealed is possibly due to some small calibration error in the feed
gas-flow rate when shifting from H₂ to D₂. Alternatively, it may be
that the equalization of the partial pressure of reactants in the gas
volume to some degree involves gas diffusion.3

The ΔZ' gas-solid peak in Fig. 6 seems to be well separated
from the other peaks (no overlap). Hence, the peak may represent a
time-invariant shift of the involved process. If the process that
is responsible for the peak is adsorption or desorption of H₂O or H₂,
a change in the active surface area would result in a time-invariant
peak. From classical statistical mechanics it is predicted that the
conductivity of D⁺ in a solid is 1/2 that of H⁺ because the “ambient
frequency” scales with 1/m, where m is the mass of the isotope. At 500 K the ratio between the H⁺ and D⁺ conductivity, σ_D/σ_H, in a
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at [<10 Hz; ~ 80 Hz; ~ 2 kHz].

Evidence for gas diffusion at the Ni/YSZ electrode was revealed
in an isotope experiment where hydrogen was exchanged with deu-
terium. The produced ΔZ’ spectrum reveals a peak around 80 Hz.

For simplicity, the high-frequency peak is referred to as a gas-solid reaction.
No evidence for diffusion was found in a $\Delta Z''$ spectrum. The enhanced resolution of processes in a $\Delta Z''$ spectrum compared with a $\Delta Z''$ spectrum is discussed in the appendix.

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### 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

$$Z(u) = \frac{R}{1 + juR} = \frac{R}{1 + x}$$  \hspace{1cm}  \[A-1\]

where $u_w = 1/RC$ and $x = juu_w$. We can now find the derivative with respect to $\ln(u)$ as

$$\dot{Z} = \frac{dZ(u)}{d\ln(u)} = \frac{dZ}{dz} \frac{dz}{d\ln(u)} = -\frac{R}{(1 + x)^2} x u = -\frac{R}{(1 + x)^2} x$$  \hspace{1cm}  \[A-2\]

#### (RQ) circuit

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

$$Z(u) = \frac{R}{1 + jRQ(u)} = \frac{R}{1 + Q}$$  \hspace{1cm}  \[A-3\]

where $u_w = (RQ)^{-1}$ and $y = (juu_w)^n$. The derivative with respect to $\ln(u)$ can be found as

$$\dot{Z} = \frac{dZ(u)}{d\ln(u)} = \frac{dZ}{dz} \frac{dz}{d\ln(u)} = -\frac{R}{(1 + Q)^2} x u = -\frac{u}{(1 + Q)^2}$$  \hspace{1cm}  \[A-4\]

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

#### Gerischer element

The impedance for a Gerischer element may be written as

$$Z(u) = \frac{R}{(1 + juu_w)^2} = \frac{R}{(1 + x)^2}$$  \hspace{1cm}  \[A-5\]

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

$$\dot{Z} = \frac{dZ(u)}{d\ln(u)} = \frac{dZ}{dz} \frac{dz}{d\ln(u)} = -\frac{R}{(1 + x)^2} x u = -\frac{u}{(1 + x)^2}$$  \hspace{1cm}  \[A-6\]

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

$$Z = \frac{R}{1 + (juu_w)^2}$$  \hspace{1cm}  \[A-7\]

and

$$Z = \frac{2R(uu_w)^2 + R(uu_w)^2[1 + (uu_w)^2]}{[1 + (uu_w)^2]}$$  \hspace{1cm}  \[A-8\]

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

$$Z'' = -\frac{2}{R}(Z')^2$$  \hspace{1cm}  \[A-9\]

where $Z''$ is the real part of $Z$ and $\dot{Z}'$ is the imaginary part of $Z$. This explains why $\dot{Z}'$ produces a sharper and more well-defined peak than $Z''$. From Eq. A-9 it is also seen that $Z''$ and $\dot{Z}'$ have a maximum (or minimum) at the same frequency. Taking the derivative of Eq. A-7 with respect to $\omega$, this frequency can be shown to be $u_w$. Figure A-1 shows a plot of $Z''$ and $\dot{Z}'$ for an (RQ)$_1$, and the Gerischer$_2$ and (RC)$_3$ elements, given the values in Table A-I, condition A.

![Figure A-1. $Z''$ and $\dot{Z}'$ for (RQ)$_1$, a Gerischer$_2$, and an (RC)$_3$, with the values specified in Table I, condition A. Note that $\dot{Z}'$ produces sharper and more well-defined peaks than $Z''$.](image)

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)Is in series, which we shall denote (RC)$_1$ and (RC)$_2$.

For such a circuit we can find

$$Z'' = \frac{-2R(uu_w)^2}{[1 + (uu_w)^2]^2}$$  \hspace{1cm}  \[A-10\]

$$Z'' = \frac{-2R(uu_w)^2}{[1 + (uu_w)^2]^2}$$  \hspace{1cm}  \[A-11\]

which also gives two peaks in a Bode plot, but the peaks are not as well separated as for $\dot{Z}'$. 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

$$\Delta Z'' = \frac{2R(uu_w)^2}{[1 + (uu_w)^2]^2} - \frac{2R(uu_w)^2}{[1 + (uu_w)^2]^2}$$  \hspace{1cm}  \[A-12\]

Now assume that an operation parameter $R'$ 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

$$\Delta Z'' = \frac{2R(uu_w)^2}{[1 + (uu_w)^2]^2} - \frac{2R(uu_w)^2}{[1 + (uu_w)^2]^2}$$  \hspace{1cm}  \[A-13\]

If $u_w' = u_w$, Eq. A-13 can be further simplified to give

$$\Delta Z'' = \frac{2R(uu_w)^2}{[1 + (uu_w)^2]^2}$$  \hspace{1cm}  \[A-14\]

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 $u_w'$, but rescaled with a factor $(R_A - R_B)/R_A$. Given the same assumptions as for the calculation of $\Delta Z''$, $\Delta Z''$ can be found as

<table>
<thead>
<tr>
<th>Table A-I. Values of the circuit elements.</th>
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<tbody>
<tr>
<td>Circuit element</td>
</tr>
<tr>
<td>(RQ)$_1$</td>
</tr>
<tr>
<td>element</td>
</tr>
<tr>
<td>Gerischer$_2$</td>
</tr>
<tr>
<td>element</td>
</tr>
<tr>
<td>(RC)$_3$</td>
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<tr>
<td>element</td>
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</table>
Figure A-2. $\Delta Z'$ and $\Delta Z''$ for $(RQ)_1$, Gerischer$_2$, and $(RC)_1$ in series, undergoing a change in $\Psi$ from condition A to B as specified in Table I. The thin lines are $\Delta Z'$ and $\Delta Z''$ for the individual elements. The inset is a plot of $Z_1$, Gerischer$^2$, and $Z_3$ in series at condition A and $Z_2$ at condition B. Looking at Eq. A-3 through A-6, it is clear that if $u''$ is preserved, the peak shape is preserved. From Fig. A-1 it is then seen that a time-variant (i.e., $u''$-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 $(RQ)_1$, a Gerischer, and an $(RC)_1$ element in series, undergoing a change in $\Psi$ from condition A to B. The elements are referred to as $(RQ)_1$, Gerischer$^2$, and $(RC)_1$, 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 $(RC)_1$ undergoes a capacitive change. Note that the three peaks are better resolved in the $\Delta Z'$ spectrum than in the $\Delta Z''$ spectrum.

References