Analysis of SOFCs Using Reference Electrodes and Deconvolution Methods

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Introduction

SOFC performance and performance degradation studies require knowledge of the separate behavior of the cathode and anode. In electrochemical testing, a reference electrode is often used in combination with a 3-electrode potentiostat. The potentiostat controls the potential between the working (WE) and reference (RE) electrodes while passing current between the WE and counter (CE) electrodes. Data acquired using this protocol should isolate the electrochemical behavior of the WE independent of the behavior of the CE.

However, the common designs of power – generating SOFCs (anode-supported and electrolyte-supported), create problems for reference electrodes. The reference electrode must be mounted on the thin electrolyte well outside the zone of ionic current flow. A number of recent papers in the literature have pointed out the problem with this configuration using simulations.[1-5] Specifically, the impedance obtained with the cathode as the WE and the anode as the CE will contain contributions from both the cathode and the anode impedances, and the amount of contribution is dependent on the cell configuration, displacement of the anode with respect to the cathode, and the frequency applied.

The purpose of this project is to confirm the predictions of the impedance simulations and to explore a potentially new method for isolating the impedance of the cathode and anode. None of the three electrode methods tried were successful.

Deconvolution of impedance spectra[6] combined with complex nonlinear regression fitting to an equivalent circuit offers more promise for identifying impedances associated with changes in gas flows and temperature. Specifically, a change in fuel concentration should affect the impedance of the anode while minimally affecting the impedance of the cathode. Similarly, changes in oxygen concentration should highlight impedances associated with the cathode.

References

1. Winkler et al., J. Electrochem. Soc. 1998, 145, 1184.
2. Adler et al., Solid State Ionics 2000, 134, 35.
3. Adler, J. Electrochem. Soc. 2002, 149, E166.
4. Cimenti et al., Fuel Cells 2007, 7, 364.
5. Cimenti et al., Fuel Cells 2007, 7, 377.
6. Schichlein et al., J. Appl. Electrochem. 2002, 32, 875.

Experimental Section

Three cell designs:

A. Anode-supported cell, 28 mm diameter, Ni/YSZ anode 0.9 mm, electrolyte YSZ 15 microns, LSM/YSZ disk cathode 50 microns by 13 mm, ring reference LSM/YSZ 40 microns, 16 mm ID x 19 mm OD.

B. FCM electrolyte-supported cell, Ni/GDC anode 13 mm x 50 microns, proprietary electrolyte 26 mm x 0.15 mm, LSM/GDC cathode, 13 mm x 50 microns, ring reference Ag paste 15 mm ID x 19 mm OD.

C. FCM electrolyte-supported cell as in B, micro-reference electrode, located within 20 microns of the cathode and with dimensions of 30 microns x 140 microns.

Gas flows: Normal : 100% H_2 fuel, 100% air. Low air: 100% H_2, 12.5% air + 87.5% N_2. Low fuel: 20% H_2 + 80% N_2, 100% air.
Temperatures: 800ºC and 700ºC.
Impedance measurements: Solartron Cell Test, EIS at OCV, 100 kHz to 0.02 Hz.

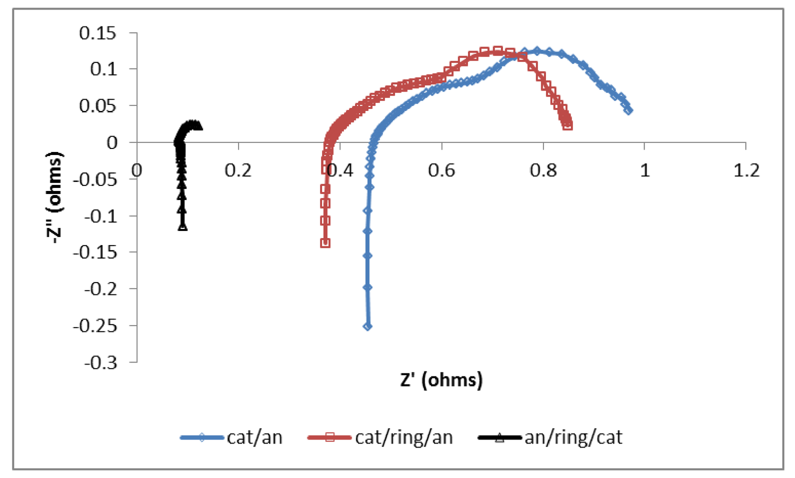

Fig. 1: Cell A, 2-electrode and 3-electrode EIS data, legend WE/RE/CE as indicated, 800ºC, normal flow.

The cat/an 2-electrode data and the cat/ring/an EIS data exhibit nearly identical arcs and polarization resistances. The an/ring/cat 3-electrode EIS data is mainly due to a series resistance and an inductance.

A very small arc appears at 0.1-1 Hz. This pattern appears for all three gas flows and for both temperatures.

This result is consistent with the simulations. The 3-electrode cat/ring/an EIS data contains impedance contributions from both the cathode and the anode. The small arc in the 3-electrode an/ring/cat EIS data is tentatively assigned to mass transfer of H_2 through the anode support layers.

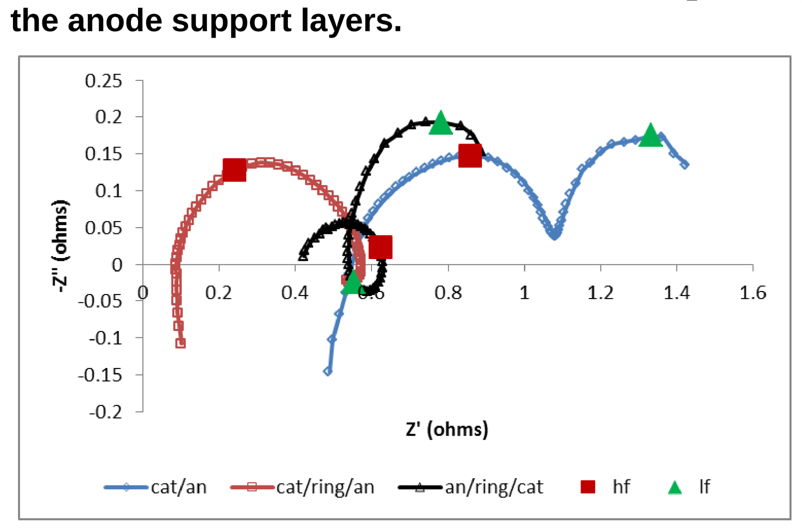

Fig. 2: Cell B, 2-electrode and 3-electrode EIS data, legend WE/RE/CE as indicated, 800ºC, normal flow.

The 2-electrode EIS plot shows 2 arcs well separated in frequency. Based on the effects of gas flow, the high frequency arc (red square, 500 Hz) is assigned to the cathode and the low frequency arc (green triangle, 0.2 Hz) is assigned to the anode.

The 3-electrode cat/ring/an EIS plot has a large arc similar to the cathode arc in the cat/an plot in frequency and polarization resistance. There is a small "inductance loop" at low frequencies. Similarly, the an/ring/cat EIS plot has a low frequency arc that matches the low frequency arc in the cat/an plot. There is a large "inductance loop" at the higher frequencies.

These plots match the simulations in Ref. 5 for a cell with 2 aligned electrodes with widely separated time constants (Case II). If the time constants (arc peak frequencies) were not widely separated, then the distortion of each 3-electrode EIS plot would be disguised.

Simulations by Dr. Celik and coworkers suggested that a micro-reference electrode within one electrolyte thickness of the cathode could potentially isolate the cathode impedance in a 3-electrode configuration.

Fig. 3 Cell C, showing the gold paste-coated cathode (right side), the glass paste insulating pad (dark grey) and the silver paste reference electrode (bright silver).

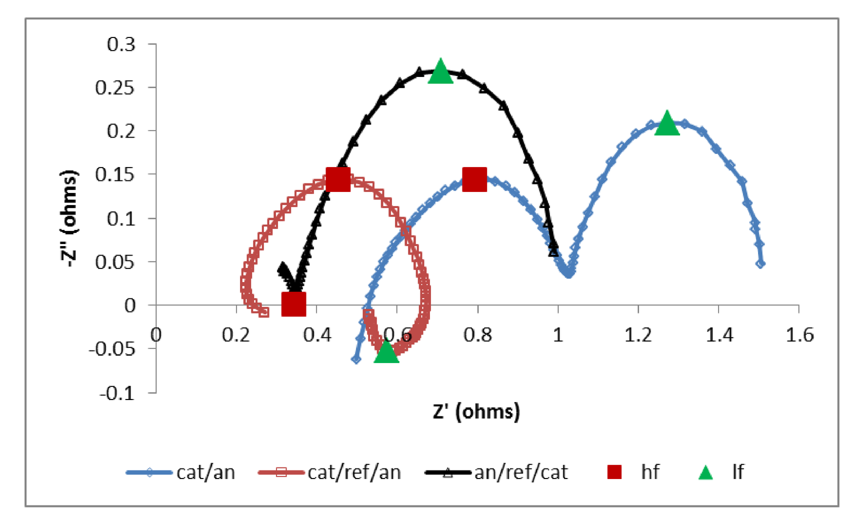

Fig. 4: Cell C, 2-electrode and 3-electrode EIS data, legend WE/RE/CE as indicated, 800ºC, normal flow.

Similar to fig. 2, each 3-electrode EIS plot shows a large arc accompanied by an "inductance loop" at either the high frequency end (an/ref/cat) or the low frequency end (cat/ref/an). Red squares mark the peak frequency for the high frequency arc (600 Hz) and green triangles mark the peak frequency of the low frequency arc (0.2 Hz) in the cat/an EIS plot.

This micro-reference electrode was not sufficiently small enough nor close enough to the cathode to isolate effectively the EIS behavior of the cathode. Smaller micro-reference electrodes are extremely difficult to fabricate and to connect to the potentiostat.

Ring electrode on the anode-supported cell

Proposed new method: Measure the 2-electrode EIS data for three pair-wise combinations of electrodes: cat/an, cat/ring, and ring/an. Assuming that each polarization resistance is the sum of the polarization resistances of each electrode, then three equations with three unknowns can be solved for the individual electrode polarization resistances:

$R_C + R_A = 0.70\ \Omega\ cm^2$
$R_C + R_R = 1.24$
$R_A + R_R = 0.86$

Solution:

$R_C = 0.54\ \Omega\ cm^2$
$R_A = 0.16$
$R_R = 0.70$

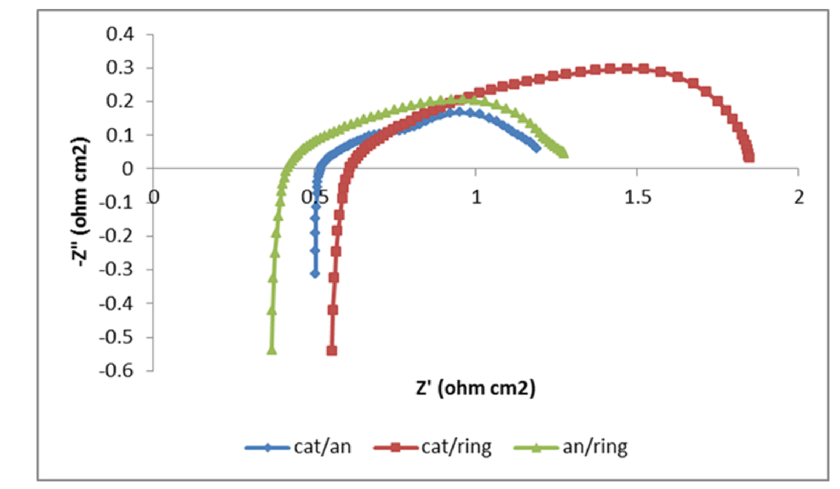

Fig. 5: Cell A, two-electrode impedances, 800ºC, normal flow.

The series resistances for the three EIS plots are similar. The cat/an and an/ring series resistances should be identical (same current density across the electrolyte); the difference is attributed to the current collectors. The similar series resistance for the cat/ring data strongly indicates a current path from cathode to the anode, along the anode, and from the anode to the ring electrode (Fig. 6).

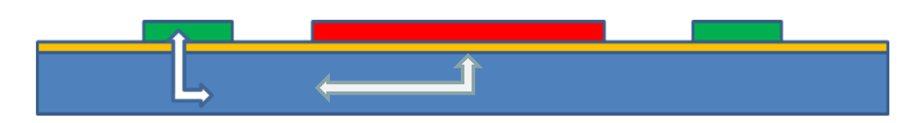

Fig. 6: Cross-section representation of Cell A, with the anode (blue), cathode (red) and ring electrode (green). The arrows show the presumed current flow for the cat/ring connection.

Flow	Cathode	Anode	Ring
800N	0.54	0.16	0.70
800LA	0.63	0.18	1.05
800LF	0.78	0.23	0.71
700N	1.20	0.28	2.14
700LA	1.94	0.49	4.73
700LF	1.62	0.36	2.58

Table 1: Calculated 2-electrode polarization resistances based on pairwise 2-electrode EIS data. Key: N = normal flow; LA = low air flow; LF = low fuel.

There are two inconsistencies. The polarization resistance for the anode increases going from normal flow to low air, and the polarization resistance for the cathode (and ring electrode) increases going from normal flow to low fuel.

Because the presumed current path for the cat/ring EIS data crosses the anode/electrolyte interface, the impedance of the anode is part of this measurement.

Summary so far:

1. As predicted, a reference electrode far from the cathode does not accurately isolate the impedance of one electrode in a 3-electrode measurement for either of the common SOFC designs.
2. A micro-reference electrode within one electrolyte thickness of the cathode does not accurately isolate the impedance of one electrode.
3. A pair-wise 2-electrode measurement for a ring electrode on an anode-supported SOFC does not provide accurate polarization resistances for each electrode.

$$Z(\omega) = R_0 + Z_{\mathrm{pol}}(\omega) = R_0 + R_{\mathrm{pol}}\int_0^\infty \frac{\gamma(\tau)}{1+j\omega\tau}\,d\tau$$

$$\text{with} \int_0^\infty \gamma(\tau)\,d\tau = 1$$

Deconvolution: Calculation of the coefficient γ, the fraction of polarization resistance between time constant τ and τ + dτ [6]. A deconvolution spectrum is a plot of γ vs frequency. A peak indicates the principal frequency of a process in the SOFC.

Equivalent circuit: Electrical circuit components designed to match the impedance and deconvolution spectrum for a data set. The most common elements are resistors and constant phase elements (CPE). Admittance of CPE = $|Y|(j\omega)^n$
A parallel combination (RQ) generates a symmetrical peak in the deconvolution spectrum with a half-width related to exponent n.
See ref. 6 for the procedure to calculate the deconvolution spectrum.

Strategy:

1. Using deconvolution, identify the main frequencies of processes in the impedance spectrum.
2. Construct an equivalent circuit.
3. Use ZView® to fit the elements of the circuit.
4. Change operating conditions (gas flow, temperature, DC voltage) and follow the changes in each parameters.
5. From changes in the fitted parameters of the equivalent circuit, associate equivalent circuit elements with the cathode and anode.

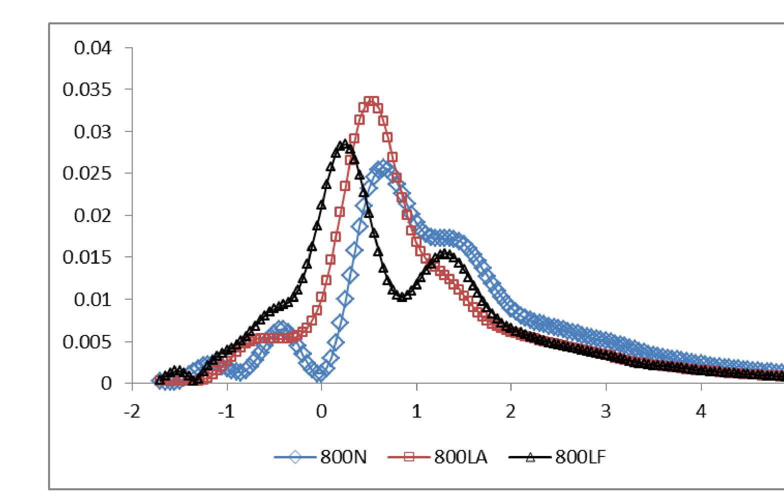

Fig. 7: Deconvolution spectra (γ vs log f) for Cell A. Gas flow conditions and temperature are in the legend.

At least 4 processes with distinct frequencies are evident. The impedance can be fitted to the equivalent circuit $Rs(R_1Q_1)(R_2Q_2)(R_3Q_3)(R_4Q_4)$.

Based on changes in frequencies and exponents for the Q elements, the following tentative assignments are proposed:

R_1Q_1 (f = 130-250 Hz, n = 0.4): anode(?)
R_2Q_2 (f = 11-21 Hz, n = 0.8) cathode
R_3Q_3 (f = 1.8-4.2 Hz, n = 1) both electrodes
R_4Q_4 (f = 0.23-0.34 Hz, n = 1) anode.

Final Summary:

Deconvolution and fitting impedances to equivalent circuits offers a method for assigning components of the impedance spectra to the cathode and the anode.

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