Electrochemical impedance analyses of solid oxide fuel cells

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ABSTRACT

Electrochemical impedance analyses are routinely applied to solid oxide fuel cells. Most commonly, the data are interpreted in terms of the ohmic resistance and polarization resistance of the SOFC through the Nyquist plot (out-of-phase impedance -Z" plotted against in-phase impedance Z') with data collected over a wide range of frequencies. More sophisticated analyses use equivalent circuits with elements that correspond to processes in the SOFC. We describe here a protocol for developing an appropriate equivalent circuit and obtaining values of the parameters of the equivalent circuit that best fit the data. The protocol uses deconvolution performed on a spreadsheet and a nonlinear regression software package. The impedance data are tested for compliance with the Kronig-Kramers transform. Compliance indicates that the impedance of the SOFC is not evolving during data collection. To separate the impedance components for the anode and the cathode from the total impedance, impedance is collected while varying the gas composition either to the anode or to the cathode. An example is given of analyses of an operating SOFC.

DATA COLLECTION RECOMMENDATIONS

(i) Minimize inductance – shortest possible leads, twisted pairs for current-carrying and voltage-sensing leads. The current and voltage lead to each electrode should be connected close to the electrode.
(ii) Collect replicate impedance data sets for any specific condition.
(iii) If collecting impedance with non-zero current, use the AC current mode with a fixed DC current.
(iv) Collect impedance data while varying the gas composition to one electrode and holding the gas composition to the other electrode constant. Assumption: only the impedance of the first electrode will change.

DATA DISPLAY RECOMMENDATIONS

Nyquist - -Z" vs Z'
Bode: Z' and -Z" vs log f

EQUIVALENT CIRCUITS

An equivalent circuit can help to identify processes associated with each electrode and to measure approximately the polarization resistance associated with each electrode. An equivalent circuit provides a means of testing the data for compliance with the Kronig-Kramers transform. Compliance indicates that the impedance of the system is NOT changing during data acquisition.
Protocol:
(i) Fit the out-of-phase impedance (Z") with equivalent circuit parameters.
(ii) Using the fitted parameters, calculate in-phase impedance (Z') for the equivalent circuit.
(iii) Adjust the ohmic resistance for the best match between Z'(data) and Z'(eq. circuit).
(iv0 Check the residuals (Z'(eq. circuit) – Z'(data)) for systematic deviations.

EQUIVALENT CIRCUIT ELEMENTS

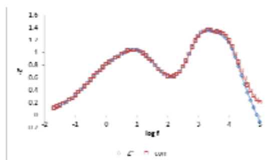
R_s – series (ohmic) resistance.
L – inductance.
Arc-generating elements:
(RQ) - Parallel combination of R (resistance) and Q (constant phase element). Represents a process whose kinetics determine R and whose reactant species concentration affects Q. Three parameters: *R*, *Q*, *n*. When *n* =1, Q is a pure capacitance.
W – Warburg (finite length). Represents diffusion over a fixed length. At high frequencies, the behavior represents semi-infinite diffusion. Two parameters: *R*, *T*.
Ge – Gerischer element. Corresponds to combined reaction and diffusion processes. Especially useful for MIEC cathodes. Three parameters: *R*, *T*, *n*.
Ideal value for *n* = 0.5, but *n* can vary.

NONLINEAR REGRESSION FITTING

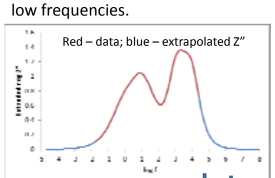
Two options:
Zview® (Scribner Associates). Requires a dongle to operate.
LEVM (available as a free download from J. Ross Macdonald's web site).
More difficult to use, but more flexible and powerful.

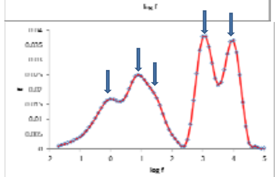
DECONVOLUTION

Used to identify an appropriate equivalent circuit and to check the fit of the equivalent circuit impedance to the impedance data. Described in Schichlein et al., J. Appl. Electrochem. 2002, 32, 875, and used by Ivers-Tiffee in many subsequent papers.
Fits the data to a Voigt equivalent circuit: $R(RC)_n$, where (RC) is a parallel resistance/capacitance combination, and n is a large number.
Output is a magnitude **g** associated with each (RC) element and its peak frequency.
Deconvolution uses the Fast Fourier Transform applied to Z" data.
To use the FFT, the Z" data must be extrapolated to zero at very high and very low frequencies.
Implemented in an Excel® spreadsheet.



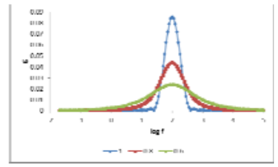
Data includes $5x10^{-7}$ H inductance.
Correct using log(Z") vs log f plot.
Use linear extrapolation of log(Z") vs log(f) to extend data to high and low frequencies.



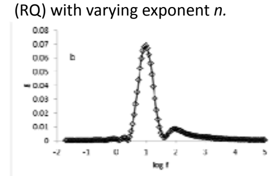


Deconvolution spectrum shows four visible peaks and a shoulder, suggesting the presence of 5 arcs. The equivalent circuit needs 5 arc-generating elements.
The shapes of the peaks guide the choice of arc-generating elements.

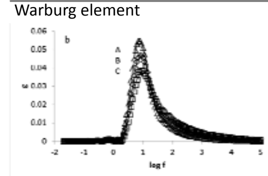
DECONVOLUTION SPECTRA OF ARC-FORMING ELEMENTS



(RQ) with varying exponent *n*.



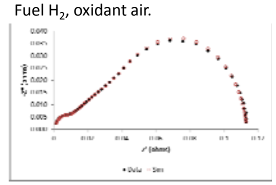
Warburg element



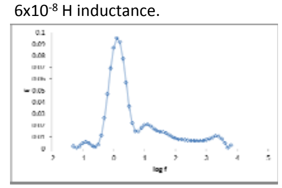
Gerischer element with exponent *n* = (A) 0.6, (B) 0.5, and (C) 0.4.

EXAMPLE

SOFC, 16 cm^2, MIEC cathode, Ni/YSZ anode. Data collected at 800ºC, OCV. Fuel H_2, oxidant air.

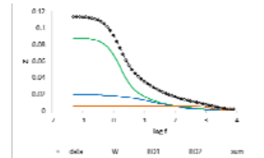


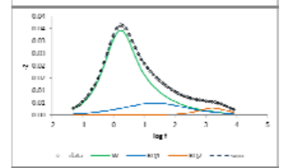
Nyquist plot. Black diamonds – data; red circles – calculated equivalent circuit impedances. Data corrected for $6x10^{-8}$ H inductance.



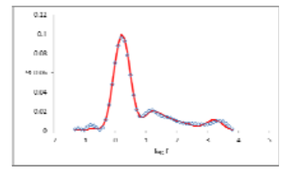
Deconvolution spectrum suggests the presence of a finite length Warburg element. Probably 2 more arcs.
Equivalent circuit LR(W)(RQ)(RQ).

EXAMPLES – QUALITY OF THE FIT

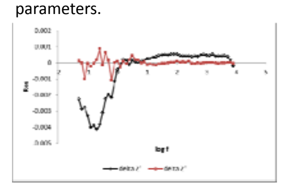




Bode plots showing the contribution of each element.

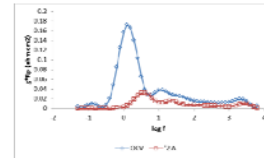


Overlay of deconvolution spectra of the impedance data (blue diamonds) and of the equivalent circuit impedance (red line). Close fits in the Bode plots and deconvolution space support the choice of equivalent circuit elements and the fitted values of the parameters.

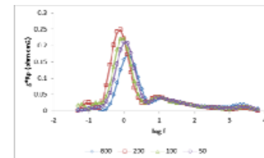


Residuals plot show a deviation in Z' residuals at low frequencies. Two possible causes: changing impedance during data collection, or errors in the impedance measurements caused by the cell + manifold. Check by collecting replicate impedance data sets.

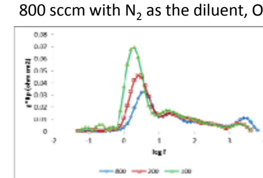
EFFECT OF CURRENT AND FUEL



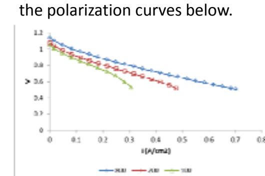
The product $g*R_p$ (polarization resistance) is used for comparisons of different conditions. In this case, 2 A (0.25 A/cm^2) current diminishes the deconvolution spectra at all frequencies. Both the anode and cathode exhibit lower impedances.



H_2 fuel flow rate in sccm, total flow 800 sccm with N_2 as the diluent, OCV.



H2 fuel flow rate in sccm, total flow 800 sccm with N2 as the diluent, 2 A current.
The low frequency peak, which is mainly associated with the Warburg element, is assigned to the anode.
The anode appears to be the cause of the mass transfer limited current in the polarization curves below.



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