DETERMINING KINETIC AND MASS TRANSFER LIMITING BEHAVIOR OF A SOLID OXIDE FUEL CELL VIA AC IMPEDANCE

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Abstract

AC Impedance has been applied to solid oxide fuel cells at various operating conditions. Experiments have been performed on small (2 cm^2) button cells and larger (61 cm^2) planar cells. Button cells were fabricated with anode and cathode reference electrodes to facilitate separate testing of anode and cathode. Impedance spectroscopy has also been applied to a five cell planar stack and to single cells therein. Equivalent circuit models are derived with each circuit element representing different processes that limit cell output. Values for the elements are obtained by fitting the model to the experimental data. The degree to which electrode kinetics and mass transfer inhibit cell output may be evaluated from the fitted resistances, capacitances, and inductances of the circuit elements. The model (including the elements used, their arrangement, and the processes to which they are ascribed) is validated by changing cell temperature, reaction rate, and reactant concentration. The presented work is useful for performing stack maintenance and diagnostics and for designing process controls and power conditioning circuitry.

Introduction

Impedance spectroscopy is a novel and powerful method to investigate the dynamic response characteristics of an electrochemical system. AC impedance is performed by superimposing an AC signal on the DC output of an electrochemical cell and measuring the impedance over a spectrum of frequencies. Equivalent circuit models, circuits of electrical elements producing a similar load response to the device under investigation, are derived from experimental data. Equivalent circuits are beneficial for stack diagnostics, because the different circuit elements theoretically represent different relaxation processes occurring in the electrochemical cell(s); hence, fit data can be used to distinguish which processes are limiting cell behavior and to what extent. In the following work, AC impedance spectroscopy has been applied to test cells and stacks at various operating conditions, and fitted equivalent circuits have been derived.

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Experimental

AC impedance was applied to solid oxide fuel cells (Ceramatec, Inc.) of two different sizes: small (2 cm^2) button cells and larger (61 cm^2) planar cells. Both consisted of a zirconia based electrolyte (~170 μm thick), a nickel based anode, and a manganite based cathode. The cells were fed at ~15 psig with air on the cathode side and mixtures of hydrogen and nitrogen bubbled through water on the anode side while varying load, temperature, reaction rate and reactant concentration. Small reference electrodes bonded to both sides of the button cell facilitated separate testing of the anode and cathode. The planar stack was fed with 1.5 SLPM air and 2.2 SLPM differing anode mixtures of hydrogen and nitrogen bubbled through water. Data were acquired at different stack currents for the cells on both ends of the stack (cell #s 1 and 5) and the middle cell (cell #3), as well as for the entire stack. All spectra collected from either cell size were fitted to equivalent circuits with Gamry's Echem Analyst software using the Levenberg-Marquardt algorithm.

Results and Discussion

Based on assumed reaction mechanisms, impedance data were analyzed in terms of equivalent circuits. Anode and cathode data of the button cell were fitted to their respective circuits to determine how reaction kinetics and mass transfer inhibits cell output. Total-cell equivalent circuits were then based on a combination of the anode and cathode models. The button cell analyses were then applied to the planar cells.

Button Cell

The overall anode reaction in an SOFC fed with hydrogen is the hydrogen oxidation reaction (HOR):

$$H_2 + O_O^{\times} \leftrightarrow H_2O + V_O^{\bullet\bullet} + 2e' \qquad (1)$$

(in Kröger-Vink notation)

Because several mechanisms [1, 2, 3, 4] are possible for the HOR, the equivalent circuit model [5], shown in Figure 1, is chosen based on the experimental data.

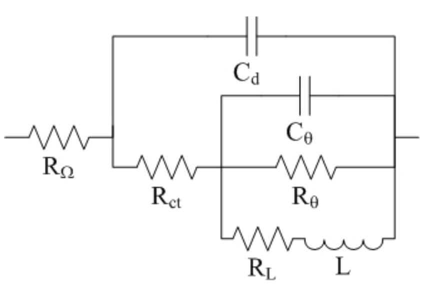

Figure 1. Equivalent circuit model for SOFC anode.

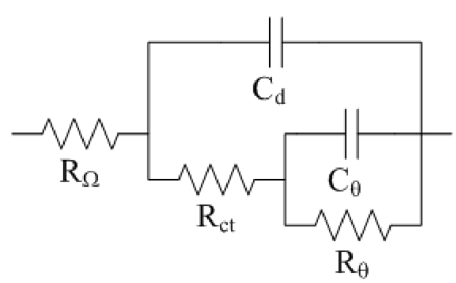

Figure 2. Equivalent circuit model for SOFC cathode.

The half reaction occurring at the cathode is the oxygen reduction reaction (ORR). Assuming a simple reaction mechanism [6, 7] of

$$O_2 + 2M \leftrightarrow 2MO \tag{2}$$

$$MO + 2e' + V_O^{\bullet\bullet} \leftrightarrow M + O_O^{\times} \tag{3}$$

(both in Kröger-Vink notation) and negligible mass transfer, a common equivalent circuit for reactions consisting of one adsorbed intermediate [8] may be derived (Figure 2); however, a CPE is expected here to replace C_d because of the variety of surfaces on which oxygen can react.

Adding the anode equivalent circuit in series with that of the cathode, a full cell equivalent circuit would theoretically be derived; however, an extra low frequency loop existed that is unique to the total-cell data. A finite diffusion element (FDE) was added to a simplified combination of the anode and cathode models (Figure 3) to fit the low frequency loop, because low frequency impedance is often attributed to concentration losses.

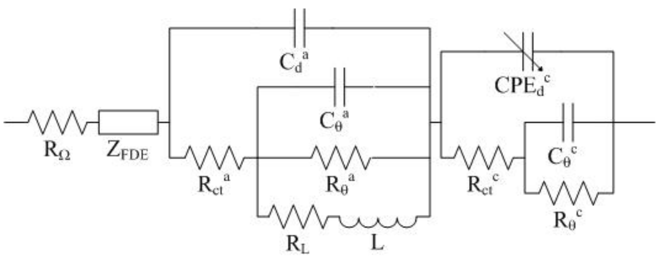

Figure 3. Equivalent circuit model for SOFC total-cell.

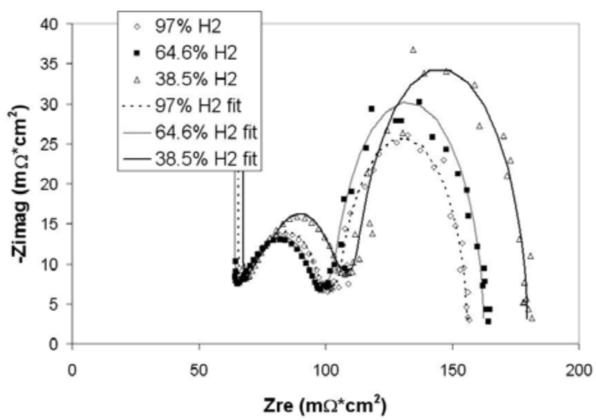

Figure 4. Prismatic cell entire stack data fit.

Prismatic cell

Theoretically, the impedance spectra of the planar cell stack would appear similarly in shape to that of the total button cell at similar operating conditions but scaled to a larger size; however, non-idealities inevitably exist as electrode areas are increased. Due to the sheer size of the cells, the current, temperature, and reactant concentration are distributed along the active surface. Additionally, the thinner bonding layers of the full cell decrease the diffusion layer thickness.

The button cell analyses were applied to the individual cells and then the entire fuel cells. The arrangement in Figure 3 was well fitted to the entire stack data (Figure 4).

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References

1. A. Bieberle, L. J. Gauckler, Solid State Ionics, 146 (2002) 23–41.
2. Wolfgang G. Bessler, J. Electrochem. Soc., 153 (2006) A1492–A1504.
3. Huayang Zhu, Robert J. Kee, Vinod M. Janardhanan, Olaf Deutschmann, and David G. Goodwin, J. Electrochem. Soc., 152 (2005) A2427–A2440.
4. V. N. Chebotin, M. V. Glumov, A. D. Neuimin, S. F. Palguev, Sov. Electrochem. Soc., 7 (1971) 55–61.
5. D. B. Zhou, H. Vander Poorten, J. Electrochem. Soc., 145 (1998) 936–945.
6. A. Lasia, in: B. E. Conway, J. O'M. Bockris, R. E. White (Eds.), Mod. Asp. Electrochem., 32, Kluwer Academic / Plenum Publishers, New York, 1999, pp. 143–242.
7. J. Deseure, Y. Bultel, L. Dessemond, E. Siebert, P. Ozil, J Applied Electrochem., 37 (2007) 129–136.
8. A. Bieberle, L. P. Meier, and L. J. Gauckler, J. Electrochem. Soc., 148 (2001) A646–A656.