Nonlinear Analysis of Porous $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ Electrodes
in Oxygen and Hydrogen-Water Environments
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$La_{0.9}Ca_{0.1}FeO_{3-\delta}$ (LCF-91) electrodes offer thermodynamically stable operation in both oxidizing and reducing ($<10^{-20}$ atm) environments relevant to SOFC/SOECs making them suitable candidates for studying the kinetic, transport, and thermodynamic phenomena dictating the overall performance of mixed conducting electrodes across a wide range of gas conditions.

In order to better understand these rate-limiting phenomena, porous LCF-91|YSZ electrochemical cells at 700-800°C were analyzed using linear and nonlinear electrochemical impedance spectroscopy (EIS and NLEIS, respectively) in both oxidizing (0.01, 0.21, 1 atm O_2) and reducing (various H_2-H_2O blends) gas environments. The data is interpreted using both one-dimensional macrohomogeneous and two-dimensional cylindrical models, similar to those used to study $La_{1-x}Sr_xCoO_{3-\delta}$ [1,2], allowing for a parallel surface diffusion pathway and altered surface thermodynamics of the electrode.

EIS data in oxygen environments, shown in Figure 1, imply a co-limitation of kinetics and diffusion. The strong p_{O2}-dependence of the peak frequency, ω_c, and the weak p_{O2}-dependence of the characteristic resistance, R_{chem}, impose constraints on possible rate-determining phenomena. However, the nonlinear response from NLEIS, such as the third-order voltage harmonic response U_{33} shown in Figure 2, is more revealing of the underlying mechanism. Using measured thermodynamic values of LCF-91 at low p_{O2} (T. Geary, S. Adler, unpublished data), analysis is extended to reducing blends of H_2 and H_2O.
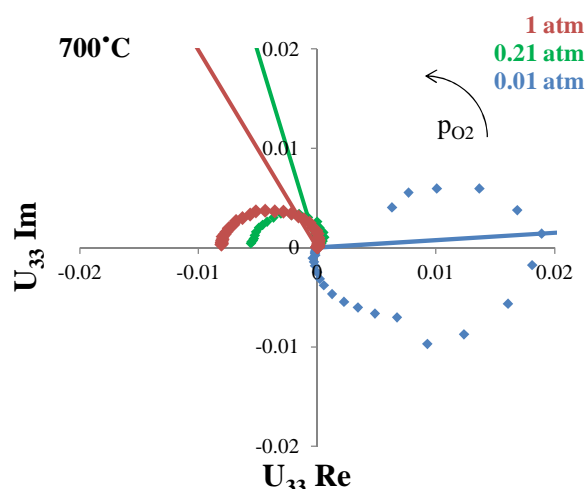

Figure 2: The measured dimensionless voltage Fourier coefficient U_{33} (corresponding to the third harmonic response of order current amplitude cubed) provided by NLEIS is very sensitive to changes in p_{O2} relative to the linear EIS response.

References

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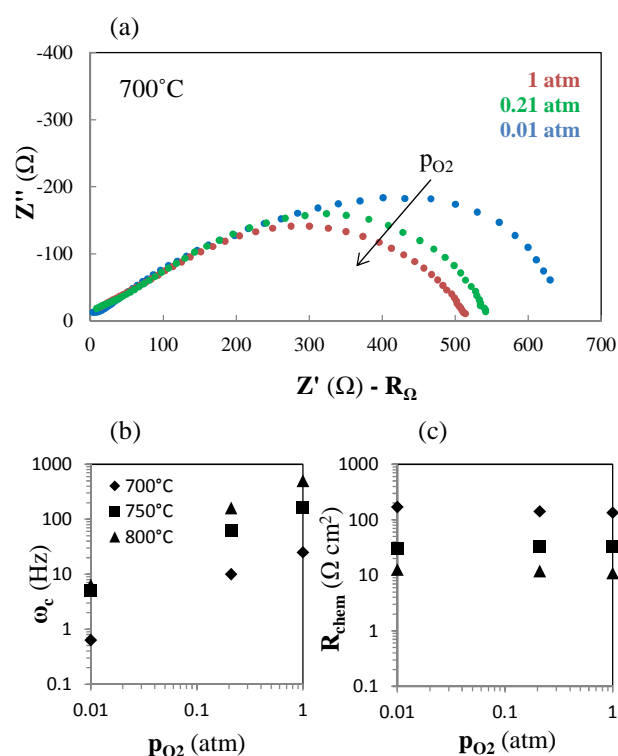

Figure 1: (a) The measured EIS response of LCF-91 half-cells after subtraction of the ohmic portion in 0.01, 0.21, and 1 atm O_2 (bal. N_2) reveals (b) ω_c to scale strongly with p_{O2}, while (c) R_{chem} remains largely p_{O2}-independent.