Nonlinear Harmonic Response of Mixed-Conducting SOFC Cathodes

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A popular technique for analyzing rate phenomena in solid-state electrochemical systems is *electrochemical Impedance Spectroscopy* (EIS), which seeks to separate and identify complex overlapping physical phenomena via *time scale*. While EIS has proven a powerful technique, it mainly difficult to fully interpret impedance response of mixed conducting SOFC cathodes due to dispersion and/or overlap among physical processes in the frequency domain, and ambiguity in interpreting linearized, low-amplitude response (often described by equivalent circuits) in terms of iverse physical mechanisms.

In order to address some of these issues, we are currently developing an extension of EIS that solves measurement and analysis of 2nd order and higher nonlinear harmonics produced by moderate amplitude a.c. perturbations. These harmonics (normally filtered-out during an EIS measurement) of noise reduction) carry substantial formation about the *nonlinearity* of physical processes. By correlating these nonlinearities to mescale, one can in principle provide unique and valuable information about the electrode reaction mechanism not available by other means. Similar techniques have been used successfully in other fields such as corrosion, biosensors, fluid mechanics, nonlinear optics, and electroanalytical chemistry.

In this paper we attempt to illustrate the usefulness of this concept by modeling the response of a dense mixed-conducting film electrode of Sr0.5Co2-xTi0.5O3 (yttria stabilized zirconia). We show that typical scenarios yielding identical impedance response have radically different behavior in the 2nd and 3rd harmonic spectra. These differences can be used to resolve overlapping effects such as bulk transport vs. surface kinetics, and isolate interfacial size laws (mechanisms) at the solid-solid and gas-solid interfaces.

As an example, Figure 1 shows the first order harmonic response (impedance) for two cases: 1) a limited 100% by ionic diffusion of oxygen through the film vs. 2) a film limited 80% by diffusion and 20% by surface kinetics. The parameters have been chosen such that both have the overall linearized d.c. resistance at zero bias. A slight phase shift is discernable between the two cases. However, the second and 3rd harmonic spectra are quite different for these two cases due to differences in asymmetry governing diffusion (thermodynamic enhancement factor) of the O reduction reaction (exponential reaction affinity).