Theory and Feasibility of Dual-Perturbation Electrochemical Impedance, Employing Simultaneous Chemical and Electrochemical Perturbations.

T.J. McDonald and S.B. Adler

University of Washington, Department of Chemical Engineering, Box 351750, Seattle, WA 98195-1750

Linear and Non-Linear Electrochemical Impedance Spectroscopy (EIS and NLEIS) are valuable tools for analysis of electrochemical materials and phenomena, due to their ability to separate individual rate processes via timescale and nonlinearity. However, like any electrochemical measurement, these techniques are inherently limited to probing *i* - *V* relationships, which for high temperature electrodes often involve a convolution of kinetic and transport rates involving multiple interfaces and materials.

In order to address this limitation, we have recently been exploring the use of a Dual-Perturbation NLEIS measurement, which utilizes a secondary modulation of reactant gas pressure to gain additional insight into solid-oxide fuel cell electrode behavior. The addition of a second perturbation expands the capabilities of EIS and NLEIS techniques in two ways:

First, in a Dual-Perturbation EIS or NLEIS experiment, the two perturbations originate at different interfaces (the pressure perturbation originating at the electrode/gas interface and the electrochemical perturbation originating at the electrode/electrolyte interface). By studying the Fourier transformed response to simultaneous perturbations (as well as beat interactions generated between the two perturbations), it may be possible to isolate portions of the response associated with each interface individually, as well as the individual contributions of mediating transport rates.

Second, by incorporating a p_{O2} perturbation directly into the time response, it is possible to directly probe the contribution of gaseous reactant concentration to the linear and nonlinear response. This allows us to measure the role of gas concentration without relying on the system being stable with time over multiple experiments. This feature is particularly important for studying systems that degrade with time, since it can be difficult to separate changes due to experimental conditions from changes caused by degradation over the course of a series of experiments.

This talk will describe the basic theory behind the Dual-Perturbation EIS/NLEIS technique, and present preliminary data establishing its feasibility.