Nonlinear Harmonic Response of Mixed-Conducting SOFC Cathodes

Stuart B. Adler, Jamie R. Wilson, and Daniel T. Schwartz
Department of Chemical Engineering
University of Washington
Seattle, WA 98195-1750

A popular technique for analyzing rate ıenomena in solid-state electrochemical systems is *'ectrochemical Impedance Spectroscopy* (EIS), ıich seeks to separate and identify complex 'erlapping physical phenomena via. *time scale*. hile EIS has proven a powerful technique, it mains difficult to fully interpret impedance sponse of mixed conducting SOFC cathodes due to .de dispersion and/or overlap among physical ocesses in the frequency domain, and ambiguity in terpreting linearized, low-amplitude response ften described by equivalent circuits) in terms of ıique physical mechanisms.

In order to address some of these issues, we are rrently developing an extension of EIS that volves measurement and analysis of 2nd order and gher nonlinear harmonics produced by moderate ıplitude a.c. perturbations. These harmonics ormally filtered-out during an EIS measurement r purposes of noise reduction) carry substantial formation about the *nonlinearity* of physical ocesses. By correlating these nonlinearities to nescale, one can in principle provide unique and .luable information about the electrode reaction echanism not available by other means. Similar chniques have been used successfully in other elds such as corrosion, biosensors, fluid mechanics, ɔnlinear optics, and electroanalytical chemistry.

In this paper we attempt to illustrate the efulness of this concept by modeling the response a dense mixed-conducing film electrode $a_{0.5}Sr_{0.5}Co_{3-\delta}$) on an oxygen ion conducting ectrolyte (yttria stabilized zirconia). We show that ıysical scenarios yielding identical impedance sponse have radically different behavior in the 2nd d 3rd harmonic spectra. These differences can be ed to resolve overlapping effects such as bulk ınsport vs. surface kinetics, and isolate interfacial te laws (mechanisms) at the solid-solid and gas-lid interfaces.

As an example, Figure 1 shows the first order rmonic response (impedance) for two cases: 1) a m limited 100% by ionic diffusion of oxygen rough the film vs. 2) a film limited 80% by ffusion and 20% by surface kinetics. The rameters have been chosen such that both have the me overall linearized d.c. resistance at zero bias. ıly a slight phase shift is discernable between ese two cases. However, the second and 3rd rmonic spectra are quite different for these two cases due to differences in asymmetry governi diffusion (thermodynamic enhancement factor) the O_2 reduction reaction (exponential reacti affinity).

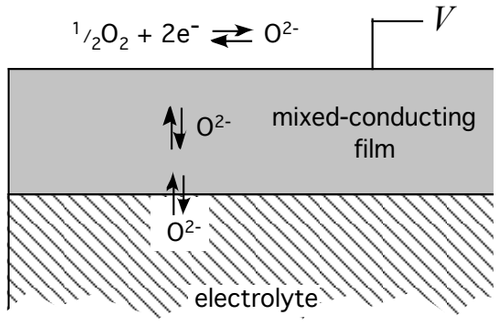

Fig. 1. First Harmonic (Impedance)

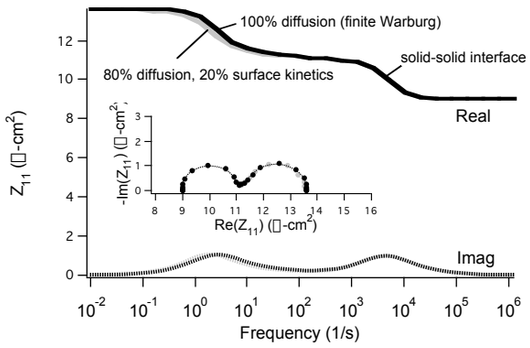

Fig. 2. Second Harmonic

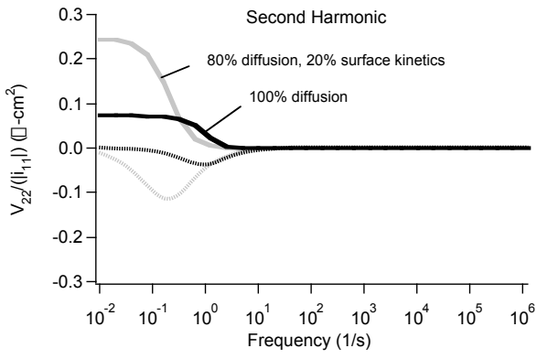

Fig. 3. Third Harmonic