Theory and Application of Nonlinear Electrochemical Impedance Spectroscopy (NLEIS).

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Traditional electrochemical impedance spectroscopy (EIS) involves measuring the linear response of an electrochemical device to a small-amplitude sinusoidal voltage or current perturbation. By quantifying response as a function of frequency, EIS can often be used to distinguish rate-limiting phenomena via *timescale*. However, a significant limitation of EIS is that it only probes the linearized response, filtering out potentially useful information contained in the frequency-dependent nonlinear response.

Over the last 7 years, our group has pioneered an extension of EIS called *nonlinear EIS*, (NLEIS) that attempts to capture this lost nonlinear information via measurement of higher-order voltage harmonics generated by a sinusoidal current perturbation [1-3]. We find that these higher harmonic signals often contain mechanism-specific features that help distinguish physical processes or rate laws governing an electrode reaction. Unlike a Tafel-slope measurement, NLEIS can be applied within a very small polarization window, mitigating voltage-induced hysteretic behavior. NLEIS is also very rubust to drift or degradation of performance because it measures and tracks the instantaneous nonlinear response, as opposed to reconstructing nonlinear behavior from multiple EIS experiments over time (where nonlinearity and time-dependence are convoluted).

This talk will review the theory behind NLEIS, and provide practical details about how we implement the measurement, as well as predict responses based on physical models. Examples will highlight results from ongoing studies of porous and thin-film mixed conducting electrodes, including analysis of degradation phenomena and analysis of O_2 reduction on inhomogeneous surfaces.

References

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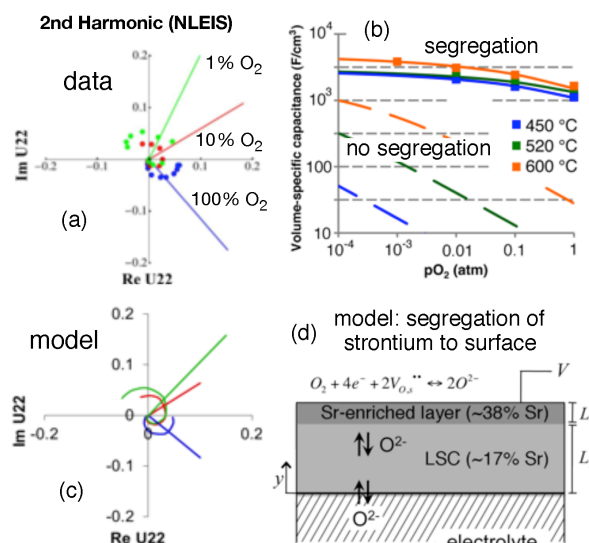
Figure 1. Use of NLEIS to diagnose electrocatalytic effects of Sr segregation within a 90 nm heteropitaxial film of $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ (LSC82) on single crystal YSZ. a) measured 2nd harmonic NLEIS response at 520°C as a function of p_{O2} (atm): 1.0 (blue), 0.10 (red), 0.010 (green). b) Faradaic capacitance of the film measured by EIS vs. T and p_{O2}. c) Calculated NLEIS response and (b) capacitance based on a the model in (d). d) Two-layer model which assumes Sr in bulk is enriched to 38% in a 15nm thick layer near the surface (as supported by SIMS measurements).
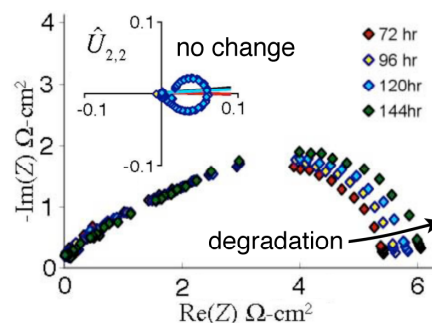

Figure 2. Time-dependent impedance (main plot) and 2nd harmonic response (inset) of a porous $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ electrode on Gd-doped ceria at 650°C and $p_{O2} = 0.05$ atm. Note that between 72 and 120 hours of operation, the electrode resistivity degrades by ~15%. Yet the normalized second harmonic remains unchanged. This result indicates that degradation is caused entirely by changes in active site density (since any change in thermodynamic properties or O_2 reduction mechanism would alter the 2nd harmonic response).