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### **Probing Local Ionic Dynamics in Functional Oxides: From Nanometer to Atomic Scale**

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Vacancy-mediated electrochemical reactions in oxides underpin multiple applications ranging from electroresistive memories, to chemical sensors to energy conversion systems such as fuel cells. Understanding the functionality in these systems requires probing reversible (oxygen reduction/evolution reaction) and irreversible (cathode degradation and activation, formation of conductive filaments) electrochemical processes. In this talk, I summarize recent advances in probing and controlling these transformations locally on nanometer level using scanning probe microscopy. The localized tip concentrates the electric field in the nanometer scale volume of material, inducing local transition. Measured simultaneously electromechanical response (piezoresponse) or current (conductive AFM) provides the information on the bias-induced changes in material. Here, I illustrate how these methods can be extended to study local electrochemical transformations, including vacancy dynamics in oxides such as titanates,  $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$ ,  $\text{BiFeO}_3$ , and  $\text{Y}_x\text{Zr}_{1-x}\text{O}_2$ . The formation of electromechanical hysteresis loops and their bias-, temperature- and environment dependences provide insight into local electrochemical mechanisms. In materials such as lanthanum-strontium cobaltite, mapping both reversible vacancy motion and vacancy ordering and static deformation is possible, and can be corroborated by *post mortem* STEM/EELS studies. In ceria, a broad gamut of electrochemical behaviors is observed as a function of temperature and humidity. The possible strategies for elucidation ionic motion at the electroactive interfaces in oxides using high-resolution electron microscopy and combined ex-situ and in-situ STEM-SPM studies are discussed. In the second part of the talk, probing electrochemical phenomena on in-situ grown surfaces with atomic resolution is illustrated. I present an approach based on the multivariate statistical analysis of the coordination spheres of individual atoms to reveal preferential structures and symmetries. The relevant statistical techniques including k-means clustering, principal component analysis, and Bayesian unmixing are briefly introduced. This approach is illustrated for several systems, including chemical phase identification, mapping ferroic variants, and probing topological and structural defects, and provides real space view on surface atomic processes. Research supported (SVK) by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division and partially performed at the Center for Nanophase Materials Sciences (AK, SJ), a DOE-BES user facility.