

Decoupling Electrochemical Reaction and Diffusion Processes in Ionically-Conductive Solids on the Nanometer Scale

Nina Balke,[†] Stephen Jesse,[†] Yoongu Kim,[‡] Leslie Adamczyk,[‡]
Iliia N. Ivanov,[†] Nancy J. Dudney,[‡] and Sergei V. Kalinin[†]

[†]Center for Nanophase Materials Sciences and [‡]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Achievement

We have developed a scanning probe microscopy approach to explore voltage-controlled ion dynamics in ionically conductive solids and decouple transport and local electrochemical reactivity on the nanometer scale. Electrochemical strain microscopy allows detection of bias-induced ionic motion through the dynamic (0.1 – 1 MHz) local strain. Spectroscopic modes based on low-frequency (~1 Hz) voltage sweeps allow local ion dynamics to be probed locally. The bias dependence of the hysteretic strain response accessed through first-order reversal curve (FORC) measurements demonstrates that the process is activated at a certain critical voltage and is linear above this voltage everywhere on the surface. This suggests that FORC spectroscopic ESM data separates local electrochemical reaction and transport processes. The relevant parameters such as critical voltage and effective mobility can be extracted for each location and correlated with the microstructure. The evolution of these behaviors with the charging of the amorphous Si anode in a thin-film Li-ion battery is explored. A broad applicability of this method to other ionically-conductive systems is predicted.

Significance

These studies hence provide previously unavailable insight into the internal functionality of Li-ion batteries, providing high-veracity, real space mapping of transport and electrochemical reactivity. The frequency-, time- and voltage spectroscopic modes of the ESM suggest the potential for performing traditional electrochemical measurements in nanoscale volumes of material. While the current studies were enabled by the intrinsic passive layer on Si surface, measurements in controlled atmosphere will allow extending this approach to other energy materials, all of which possess high $c(\text{Li})$ – strain coupling. Furthermore, given that the chemical expansivity, i.e. changes in material volume as a function of the concentration of a mobile component (metal cation, oxygen vacancies) is ubiquitous feature of all ionic and mixed ionic-electronic conductors and has been demonstrated for ceria, cobaltites, nikelates, and manganites, the ESM imaging and spectroscopy can be expected to be broadly applicable for these materials and corresponding devices (fuel cells, batteries, electroresistive electronics) as well.

Credit

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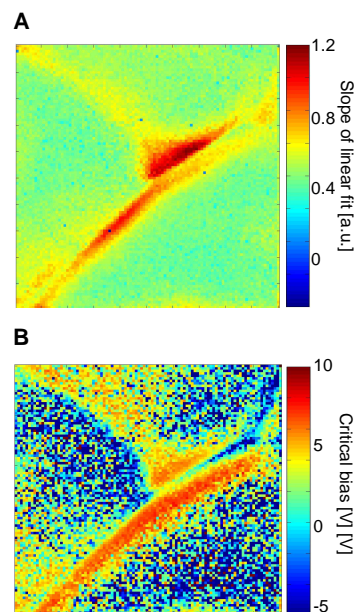


Fig. 1. Separation of reaction and transport phenomena. **(A)** Slope a and **(B)** Critical bias.