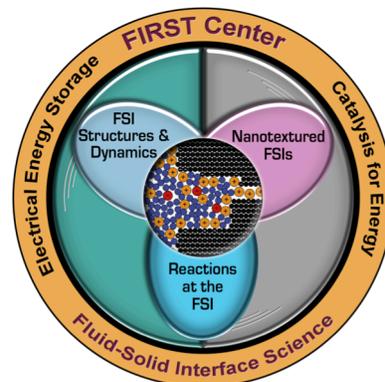


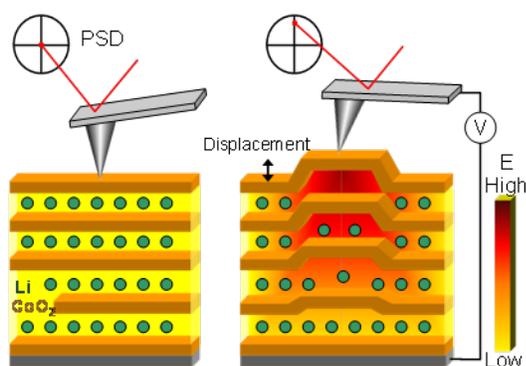
## FIRST Center Research Perspective:

### *Electrochemical Strain Microscopy*

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**Research Summary:** We have suggested and developed an Electrochemical Strain Microscopy approach to explore voltage-controlled ion dynamics in ionically conductive solids and decouple transport and local electrochemical reactivity on the nanometer scale. In ESM (**Figure 1**), a biased SPM tip concentrates an electric field in a nanometer-scale volume of material, inducing an interfacial electrochemical process at the tip-surface junction and diffusive and electromigrative ionic transport through solids. The intrinsic link between the concentration of ionic species (and/or oxidation states of the target cation) and molar volume of the material leads to electrochemical strain and surface displacement, which can be readily detected by scanning probe microscopy (SPM) electronics in the form of time- and voltage dependence responses. Probing these as a function of position creates a map of local electrochemical and ionic activity, often with sub-10 nm resolution.

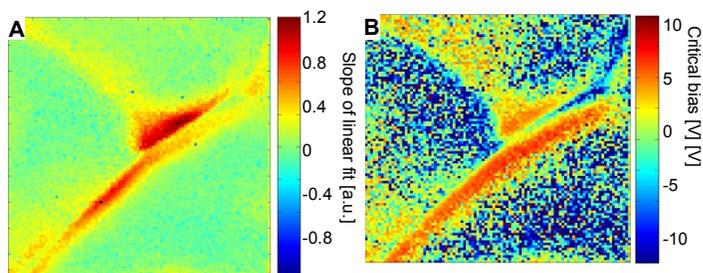


**Figure 1** ESM: Inducing local Li-ion transport in a layered cathode material through a biased atomic force microscopy tip.

**Technical Details:** The ESM approach was first suggested theoretically in [1]. The analytical solutions for ESM contrast in diffusionally-coupled reaction process are reported in [2]. This analysis has demonstrated that detection limits in ESM offer  $10^6$ - $10^8$  decrease in signal generation volume compared to classical electrochemical strategies based on Faradaic current detection, thus suggesting that ESM was, at the time, a high-risk, but potentially very high reward research direction. The ESM was demonstrated experimentally for a variety of electrochemically-active model systems, most notably  $\text{LiCoO}_2$  cathodes [3] and Si anodes [4]. In  $\text{LiCoO}_2$ , we demonstrated the ESM method and voltage spectroscopy as well as performed initial analysis of image formation mechanisms. It was possible to identify grains and grain boundaries with enhanced Li-ion kinetics (**Figure 2**). Subsequently, using model amorphous Si anode (a-Si) surfaces, the local Li-ion flow and the microstructure of a  $\text{LiCoO}_2/\text{LiPON}/\text{a-Si}$  all-solid thin film battery was investigated. It was found that the microstructure, which showed grain-like features

separated by boundaries, is strongly correlated with the Li-ion transport through the amorphous Si anode. Topography trenches show an enhanced Li-ion content after applying electrical bias to the battery, suggesting the existence of Li-ion conduction channels [4] and opening the pathway towards exploring the evolution of Li-ion dynamics as a function of charge state of batteries during operation. In both cases, rapid progress was possible due to extensive prior instrumental development at ORNL's Center for Nanophase Materials Science (CNMS) (S. Jesse and S.V. Kalinin, CNMS research), as well as availability of high-quality samples, through FIRST center collaborative interactions. Both factors were crucial in achieving this progress.

These first demonstrations of ESM have stimulated ongoing efforts in description of corresponding image formation mechanisms on the *mesoscopic* level, with the ultimate goal of rendering ESM *quantitative* in the same sense as the potentiostatic intermittent titration technique (PITT) or electrochemical impedance spectroscopy (EIS). Given practical limitations, to date we have focused on analytical models and phase-field numerical simulations. The phase-field modeling of ESM contrast as a function of local crystallographic orientation is reported in [5]. The generalized point force/source solution for ESM problem is developed in [6]. We are now exploring the theoretical aspects of ESM as a crucial task toward making the method truly quantitative and linking measured responses to specific electrochemical functionalities (surface reaction rates, diffusivity, mobility). The ESM technique was further extended to a range of spectroscopic techniques that allow real-space mapping of the diffusion and electrochemical phenomena in solids. The use of low-frequency ( $\sim 1$  Hz) voltage sweeps allow ion dynamics to be probed locally, since these time scales are directly comparable with diffusion times of ions on the 1-10 nm length scale [4].



**Figure 2.** Separation of reaction and transport phenomena in a-Si. (A) Slope  $a$  is proportional to corresponding mobility. (B) Critical bias defines the potential for reaction onset.

**Significant Impacts on Science and Technology:** The development of advanced energy storage systems including batteries and supercapacitors with high energy and power densities and intrinsically long life times is one of the highest priorities for DOE. Operation of such systems involves multiple steps of (a) ionic transport to the surface induced by an external electromotive force or chemical potential differences and affected by the structure of the surface double layer, (b) binding to the surface with the loss of solvation sphere and (c) potential intercalation into the solid matrix with charge transfer to the solid, with subsequent (d) electronic and (e) ionic transport and potentially phase transformations of the solid matrix. Any of these steps can be the rate limiting, thus determining the power density of the material. Furthermore, local deviations from equilibrium associated with local overpotentials and strains, will ultimately be responsible for the life times and failure modes. These considerations bring forward the challenge of characterizing the electrostatic, ionic, electronic, mechanical and electrochemical phenomena at

the solid–liquid interface locally on the level of a single nanopore, step edge, or structural defect. Unless the limiting steps controlling the rates of charge and discharge processes and potential failure points are identified and correlated with microstructure on the level of *individual* structural elements, the knowledge-driven design and optimization is hardly possible. Furthermore, once available on the nanometer scale, such knowledge provides a much-needed bridge between the macroscopic electrochemical behavior and local density functional and molecular dynamic modeling. Electrochemical Strain Microscopy offers the potential for nanometer-resolution functional imaging and relatively high throughputs, thus rendering it a powerful tool to study electrochemical phenomena in these materials and devices both under *ex-situ* and *in-operandi* conditions. It is also relevant to note that ESM technique was patented and technology was licensed by Asylum Research, and this methodology is now available to general CNMS users through peer-reviewed proposals.

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