Electrochemical Strain Microscopy: An Innovative SPM Technique for Energy Storage Research and Development

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INTRODUCTION

Electrochemical strain microscopy (ESM), developed by the Oak Ridge National Laboratory and Asylum Research Corporation, is an innovative scanning probe microscopy (SPM) technique capable of probing electrochemical reactivity and ionic flows in solids on the sub-ten-nanometer level, three to four orders of magnitude below the effective resolution of conventional electrochemical methods. While scanning tunneling microscopes (STMs) measure electronic currents and atomic force microscopes (AFMs) measure forces, ESM is the first technique that measures ionic currents, providing a new tool for mapping electrochemical phenomena on the nanoscale.

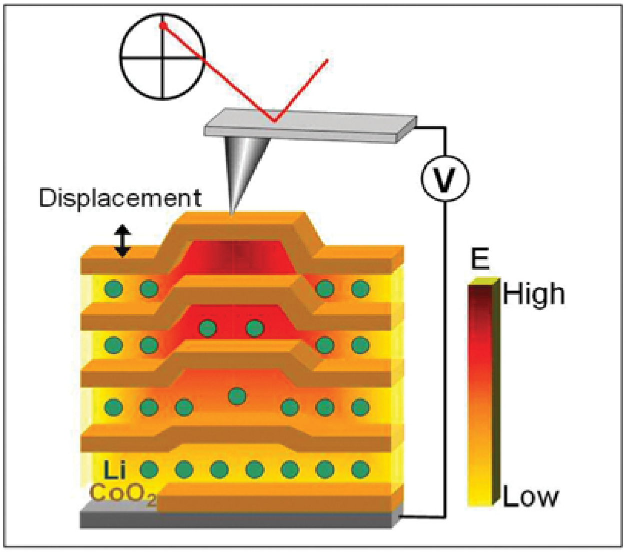

Figure 1: Principle of Electrochemical Strain Microscopy
During electrochermical strain microscopy (ESM), a periodic bias is applied to the scanning probe microscope (SPM) tip in contact with the sample surface. The applied bias induces ionic motion in the sample and the resulting surface deformation is detected by the SPM electronics, generating an image that maps the ionic motion at the nanoscale.

ELECTROCHEMICAL STRAIN MICROSCOPY

In ESM, a biased SPM tip concentrates an electric field in a nanometer-scale volume of material, inducing interfacial electrochemical processes at the tip-surface junction and ionic currents through the solid (Figure 1). The intrinsic link between concentration of ionic species and/or oxidation states of the host cation and molar volume of the material results in electrochemical strain and surface displacement. The sensitivity of standard SPM platforms allows for detection of ~2 to 5 picometer surface displacements in the ~0.1 to 1 MHz frequency range, which allows the theoretical detection limits to be estimated as ~20% changes in lithiation state within one unit cell (i.e. elementary volume of material) for materials such as $LiCoO_2$ (the most common cathode component).

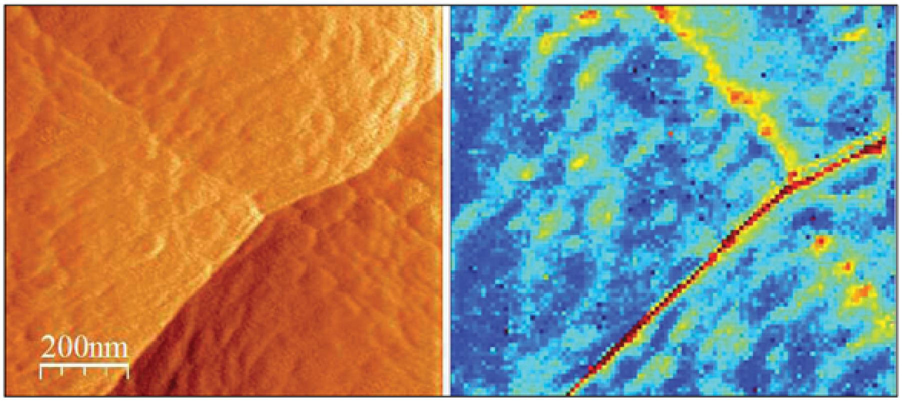

Figure 2: Mapping of Lithium Ion Diffusion.
The topographic image (left) of amorphous silicon anode in the Si/LiPON/$LiCoO_2$ thin-film battery structure shows the presence of a number of grain boundaries, as well as extensive surface roughness. The ESM image (right) is obtained by measuring the electrochemical strain hysteresis loops at each pixel (100x100 pixel image over a 1 μm area). The area hysteresis loop is a measure of lithium-ion mobility, and is plotted as a 2D map (dark blue corresponds to closed loops, red to open loops). The enhanced lithium-ion mobility along the sharp grain boundary is clearly seen, as well as localized hot spots on the diffuse grain boundary and within the grains. The effective spatial (leteral) resolution of ESM for this material is ~10 nm, providing a high-resolution view of lithium-ion dynamics in these materials. (Reprinted from Reference 4).

APPLICATIONS

The capability to probe electrochemical processes and ionic transport in solids is invaluable for a broad range of applications for energy generation and storage (batteries, fuel cells). The viability of electric vehicles and grid storage as key components of renewable energy technology hinges on advances in battery energy densities and lifetimes. ESM has the potential to aid in these advances with two major improvements over other current technologies: (a) the resolution to probe nanometer-scale volumes and (b) imaging capability extended to a broad range of spectroscopy techniques.

To date, ESM has been demonstrated for a variety of lithium-ion materials, including layered transition metal oxide cathodes, silicon anodes, and electrolytes such as LISICON; oxygen electrolytes, including yttria-stabilized zirconia (YSZ) and samarium-doped ceria; mixed electronic-ionic conductors for fuel cell cathodes; and some proton conductors (Figure 2). In addition, because electrochemical strains are ubiquitous in virtually all solid-state ionics, ESM will be applicable to all battery and fuel cell materials in energy technologies, as well as ionic-based memory and information technology devices.

REFERENCES

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