

Operando EC-AFM Imaging of Li-O₂ Battery Solid-Electrolyte Interphase



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It is commonly understood that batteries are electrochemical devices that feature electrical currents, internal ion flows, and chemical reactions. It may be less obvious that batteries also undergo structural changes during their charge and discharge cycles. Yet these changes have a critical effect on battery performance and especially battery lifetime. One reason these structural changes are sometimes overlooked is that they are surprisingly difficult to measure. After all, for most battery architectures it is not possible to “look” inside with an *operando* measurement, that is, a measurement that takes place during actual operation. Most microscopy techniques, including light microscopy and electron microscopy, cannot visualize what happens inside an operational battery. Atomic force microscopes (AFMs), however, provide a solution wherein model battery systems can be measured during operation. AFMs like the Asylum Research MFP-3D and Cypher ES are available with electrochemical cells, which enables AFM imaging while also allowing the electrochemical reaction to take place. This mode of operation is known as Electrochemical AFM imaging, or just EC-AFM.

For lithium (Li) battery technologies, we know from post-operation analysis that a chemistry-dependent solid-electrolyte interphase (SEI)

generally forms and dissolves during discharge and charge cycles, respectively. In the schematic of a generalized Li battery in Figure 1, the interfaces of interest for SEI formation are highlighted. However, little is known about the structural evolution of this SEI as a function of time, charge state, and cycle number. Crucially, SEI structure influences current density, battery capacity, achievable output voltages, operational lifetime, and even safety. So, understanding SEI evolution will help make better, longer-lasting, safer batteries.

Other issues make this research even more complex. Lithium metal is unstable in environments containing oxygen, nitrogen, water, and other volatile and reactive molecules. So for safety and proper battery operation, Li batteries are usually assembled and tested in dry, argon-filled gloveboxes. Also, the proprietary solvents and electrolyte blends used in batteries (organic carbonates, ionic liquids, organic-soluble salts, etc.) can be toxic, flammable, still under development, or poorly characterized.

Successfully navigating these challenges requires an AFM with a well-controlled environment to successfully image the dynamics of electrodes and charge-transfer interfaces in batteries in realistic operating conditions. Enter the Cypher ES AFM with

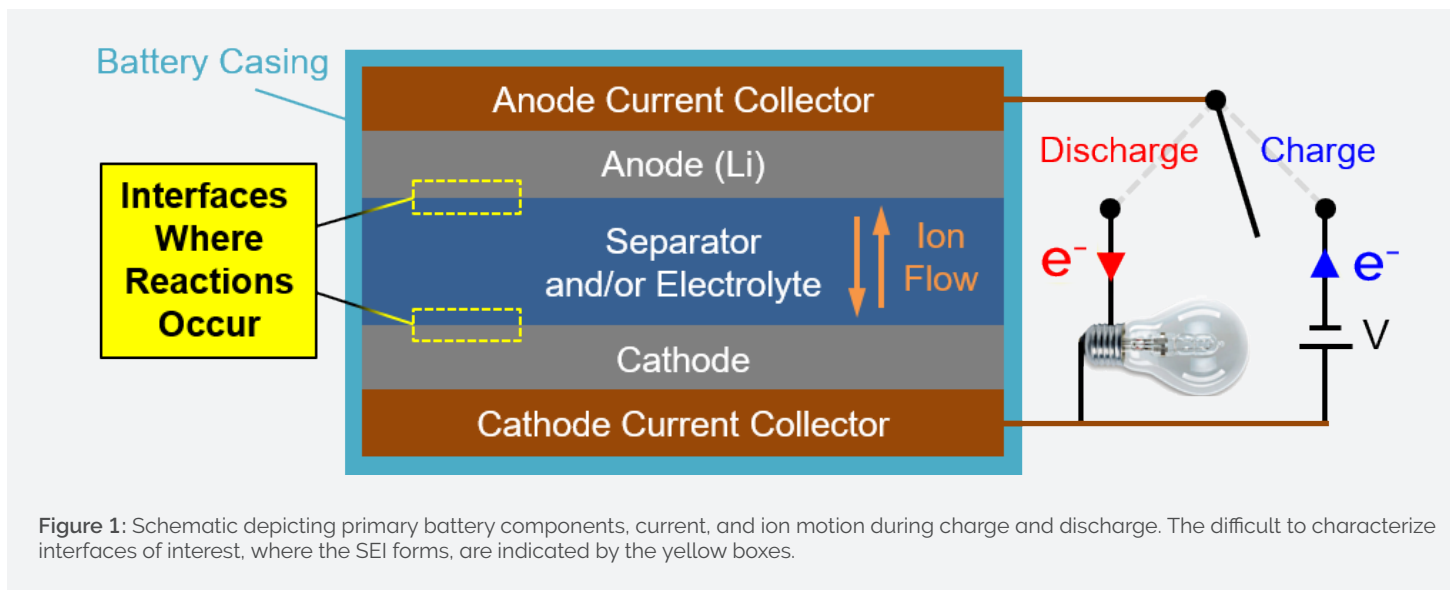


Figure 1: Schematic depicting primary battery components, current, and ion motion during charge and discharge. The difficult to characterize interfaces of interest, where the SEI forms, are indicated by the yellow boxes.

its accompanying Electrochemical Cell (EC cell) from Oxford Instruments Asylum Research.^{1,2} As shown in Figure 2, the Cypher is straightforward to integrate with an argon glovebox, and its environmental chamber allows for further atmospheric control locally around the sample. Meanwhile, the EC-specific probe holder lets the AFM probe dip down into an electrolyte bath, making it possible to image coin-cell-type battery geometries.

One of Asylum's experienced users, Dr. Kumar Virwani used exactly this instrumentation at IBM Almaden Research Center to obtain the electrochemical AFM (EC-AFM) data presented below. He took advantage of the intense reactivity of Li towards oxygen and water to investigate Li-O₂ batteries modeled after those in a previous study.³

In Figure 2, one may notice that oxygen seems to be flowing directly into the glovebox. That would normally run counter to the whole purpose of a glovebox and create a hazardous situation. However, the fully-sealed Cypher ES sample chamber and tubing keep the in-flowing oxygen separate from the glovebox atmosphere, even at positive oxygen pressure relative to the glovebox interior. This allowed Dr. Virwani to cycle Li-O₂ batteries for up to a week and monitor the *operando* evolution of the cathodic SEI as a function of time and charge state. Figure 3 shows EC-AFM images of the

cathode surface of such a battery at various points in a single discharge/charge cycle lasting about ten hours. In these measurements, the probe is a non-perturbative observer of the topography; it remains electrically floating and uninvolved in the chemical reaction.

These data suggest that, in the early stages of discharge, the SEI, a mixed-valence Li_xO_y material, first nucleates in solution as large spherical/toroidal structures (Figure 3B), followed by the nucleation of smaller nanostructures on the cathode surface (Figure 3C). The spherical/toroidal shape of the large deposits is consistent with previous scanning electron microscopy results⁴ and is in part mediated by H₂O molecules in the solvent.⁵ Cathodic nanostructures continue to increase in size during discharge, completely filling the spaces between large deposits by the time discharging is complete (Figures 3D-G). Upon charging, the structures initially persist (Figure 3H), then begin to dissolve (Figure 3I), and finally disappear by the time 50% state of charge is reached (Figures 3J and K).

Dr. Virwani's article discusses these conclusions in much greater depth. It also shows: (1) EC-AFM data acquired with varying water concentration, (2) compelling videos of the SEI evolution obtained through extended *operando* EC-AFM imaging, (3) impedance spectroscopy, and, (4) SEI volumetric analysis.⁶

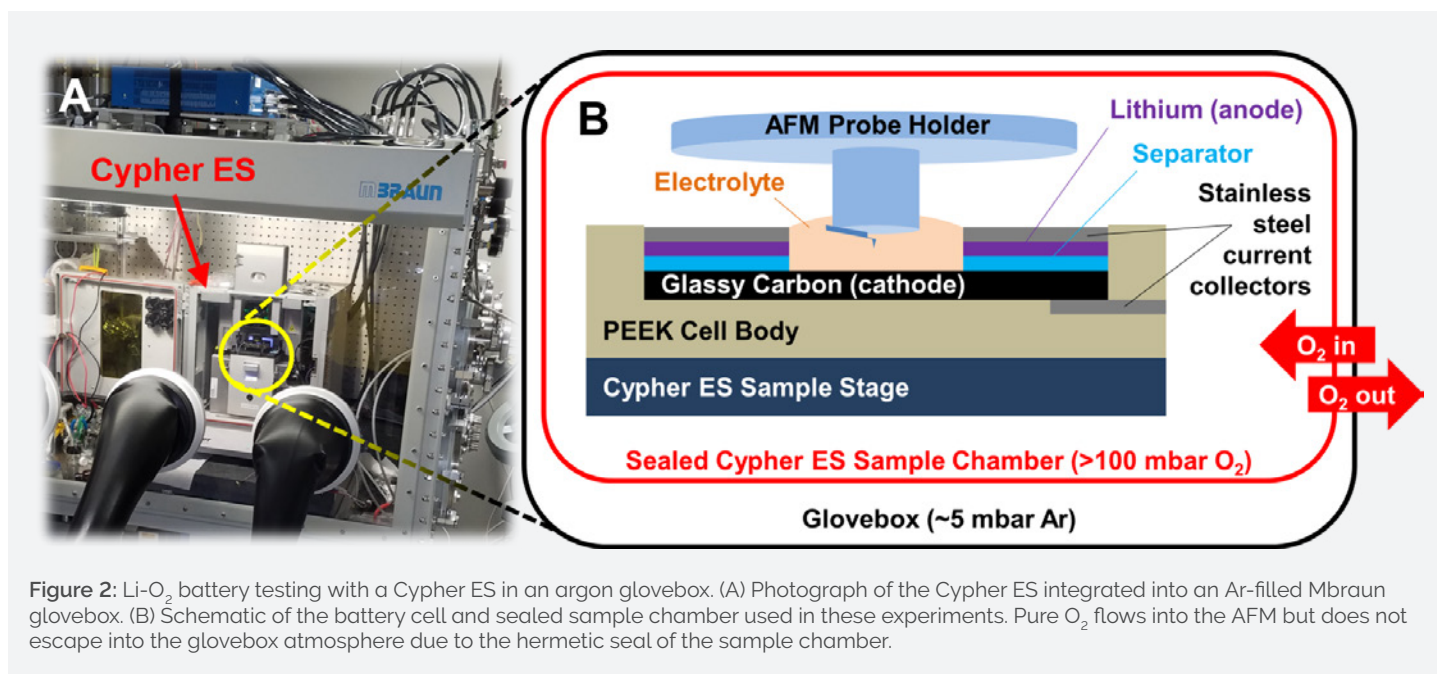


Figure 2: Li-O₂ battery testing with a Cypher ES in an argon glovebox. (A) Photograph of the Cypher ES integrated into an Ar-filled Mbraun glovebox. (B) Schematic of the battery cell and sealed sample chamber used in these experiments. Pure O₂ flows into the AFM but does not escape into the glovebox atmosphere due to the hermetic seal of the sample chamber.

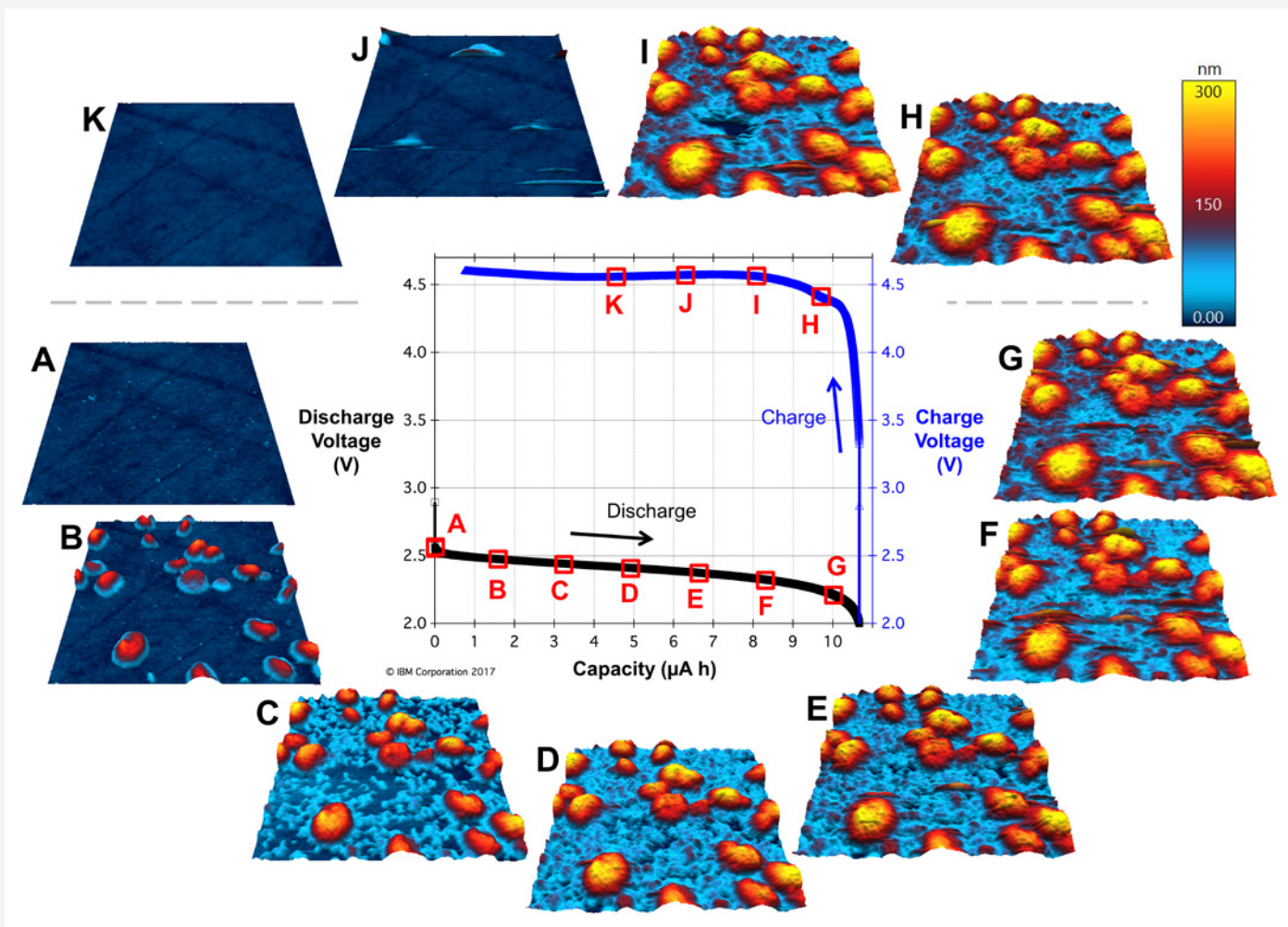


Figure 3: Li-O₂ battery cycling and *operando* EC-AFM images. In the center is the discharge/charge voltage cycle plotted against the capacity, surrounded by tapping-mode images of the cathode SEI topography obtained at the timepoints A-K indicated in the cycle. The cathode was polished glassy carbon, the anode was Li metal, the solvent was tetraglyme, the electrolyte was 1 M LiNO₃, and the discharge/charge rate was 5 µA, corresponding to a full cycle time of ~10 h. The scan size is 3 µm x 3 µm and the height scale is 300 nm for all images.

Examples of similar *operando* battery imaging are rare. This is no doubt limited by the fact that most AFMs cannot be configured with experimental conditions that mimic real battery chemistry. However, examples are emerging now that this EC-AFM capability is present on the Cypher ES. In one recent notable example, sodium oxide (NaO₂) batteries were analyzed with EC-AFM on the Cypher ES. It was found that the stability of the NaO₂ discharge products in the electrolyte could help explain the high cyclability of the battery.⁷ These measurements were possible thanks to the exquisite control of Cypher ES with the EC cell accessory and suggest this technique could readily be extended to other sensitive electrochemical measurements requiring extraordinary environmental control.

Our society is becoming increasingly reliant on mobile devices and batteries and electric motors are gradually supplanting internal combustion engines in vehicles and machinery for their reduced environmental impact. These changes have made batteries with improved capacity, safety, and economy more important than ever before. Asylum Research AFMs provide a unique capability to study battery systems *operando*, providing new insights that will drive new energy storage innovations.

References

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