

Improving Battery Performance with AFM



ASYLUM RESEARCH

Batteries power a lot of our modern technologies from cell phones to laptops. In the late 20th century, development in battery technology was mainly motivated by the rise of such portable consumer electronics, which required batteries of high energy density.¹ This gave rise to the wide use of rechargeable nickel-cadmium batteries; but by the 1990s, lithium ion batteries (LIBs) had taken over as the dominant technology. Lithium has low molecular weight, low density, and it intercalates into various layered materials, resulting in a high volumetric energy density (200 W h L^{-1}) twice that of competing systems at the time. The last three decades saw an impressive increase in capacity to more than 400 W h L^{-1} , which spurred the rapid reduction in size of portable devices we witnessed over this period.

LIBs are based on the transport of Li ions across the battery cell; for example, during discharge, lithium ion flows from the anode to the cathode, providing current that powers devices.² Lithium metal oxides like LiCoO_2 (LCO) are favored cathode materials due to their high chemical potential (vs. L/L^+), while graphite is favored as a low voltage anode material for its layered structure, natural abundance, and low cost.³ It was also important to develop non-aqueous electrolyte solutions such as propylene carbonate or ethylene carbonate that allowed for reversible lithium intercalation with minimal capacity fade.⁴ Critical in this development is understanding the role of the solid electrolyte interface (SEI), which forms a passivating layer that protects the metallic form of lithium. Performance of the SEI directly impacts the aging of battery cells, and the total number of charge-discharge cycles.

To improve overall performance, all aspects of the battery device need to be understood and optimized. The cathode and anode materials, the separator, and the electrolyte, including the formation of the SEI, are all potential targets for engineering to improve energy and power densities, as well as aging.

Atomic force microscopes (AFMs) provide a way to visualize battery materials at micro and nanometer resolutions in order to evaluate their texture and morphology—to better understand, for example, how their processing can impact performance. In addition, AFMs can be used in nanoelectrical and nanomechanical characterization to provide insight on how material properties can be engineered at the

nanoscale. Unlike other characterization tools, AFMs can also be operated within inert atmosphere (e.g., in a glovebox), and measurements can be done in situ or in environments (e.g., in electrolytes) relevant to the operation of the battery cell.

The following examples show how AFMs can be used to evaluate materials from different parts of the battery cell to provide critical information in improving their overall performance.

Aging of LiCoO_2 (LCO) Cathodes

A continuing challenge in battery research is the reduction in capacity fade over a larger number of charge/discharge cycles. Understanding aging of battery materials at the microscopic level is key to improving their performance in this regard. AFMs can monitor the evolution of critical properties with high spatial resolution, which can give insight into the degradation of material performance. AFM has been used to study the evolution of contact stiffness and surface potential of lithium cobaltate (LCO) thin films as a function of charge/discharge cycle, which has yielded insights on the aging behavior of this important cathode material.⁵

Fig. 1 shows how LCO thin film roughness, grain size, and contact stiffness evolve over 100 charge/discharge cycles. AFM nanomechanics, typically utilizes indentation techniques which are slow and plastically deform the sample. Here, researchers used AM-FM Viscoelastic Mapping mode, a tapping mode based technique proprietary to Asylum Research, which obtains both surface morphology and contact stiffness simultaneously. Imaging is therefore fast and high resolution, as well as gentle on the sample because it relies on monitoring small frequency shifts to map out contact stiffness.

Surface roughness and grain size increases with the number of charge/discharge cycles, while contact stiffness decreases. Furthermore, while roughness and grain size increase linearly, there is a more rapid decrease in contact stiffness in the first 10 cycles, which becomes less pronounced at higher cycle numbers.

Changes in grain size has been shown to be induced by changes in the structure of LCO due to the intercalation and deintercalation of lithium ions during the charge/discharge process. The change

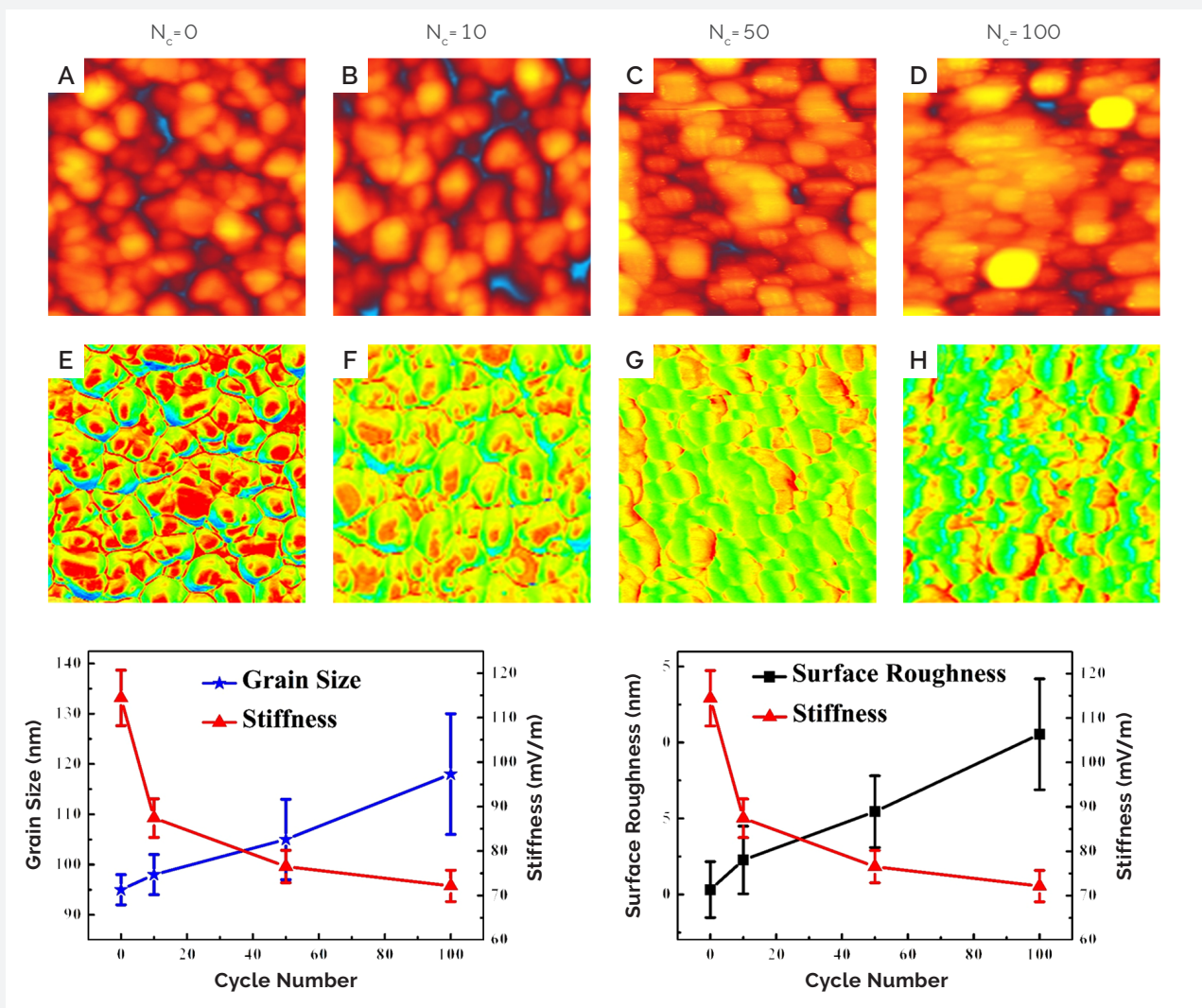


Figure 1: Evolution in surface morphology (A-D) of LCO cathode films, and their contact stiffness (E-H), measured by AM-FM viscoelastic mapping mode, as a function of the number of charge/discharge cycles. The bottom graphs show that while grain size and surface roughness increased linearly, contact stiffness decreased more dramatically in the first 10 cycles.

in dimensions is anisotropic, and because the grains are bounded by each other, stress is generated between grains. Local changes in lithium ion content also produce defects which results in stress. These accumulate over the number of cycles resulting in fracture and agglomeration into bigger grains, which is confirmed in roughness and grain size trends.

It is known that the lithiated form of LCO is stiffer than the delithiated form. Before cycling, the edges of the grains are less stiff than the center, and indeed these are expected to have more lithium ion content. When the battery is charged, the cathode is delithiated, and subsequently re-lithiated during discharge. A decrease of stiffness over time indicates that lithiation is not completely reversible, resulting in reduction in capacity. Furthermore, it is also known that the SEI, which forms during the first few cycles, is responsible for elastic modulus degradation of cathode films. This may be the reason for the initial dramatic decrease in contact stiffness observed during the first 10 cycles.

In addition to contact stiffness, surface potential, measured by Kelvin Probe Force Microscopy (KPFM), also evolves over 100 charge/discharge cycles. Fig. 2 shows a similar trend where grain size increases linearly while surface potential dramatically decreases in the first 10 cycles, followed by a more gradual decrease until 100 cycles.

The work function of LCO is higher in the lithiated form, than in the delithiated form. Since the intercalation/deintercalation is not completely reversible, the surface potential decreases over the number of cycles since both phases become present and coexist in the film. Surface electrochemical reactions and coarsening of the nanograins can also contribute to the lower surface potential. The surface potential distribution also becomes more uniform over the number of cycles, indicating a more even distribution of lithium ions with higher cycle numbers.

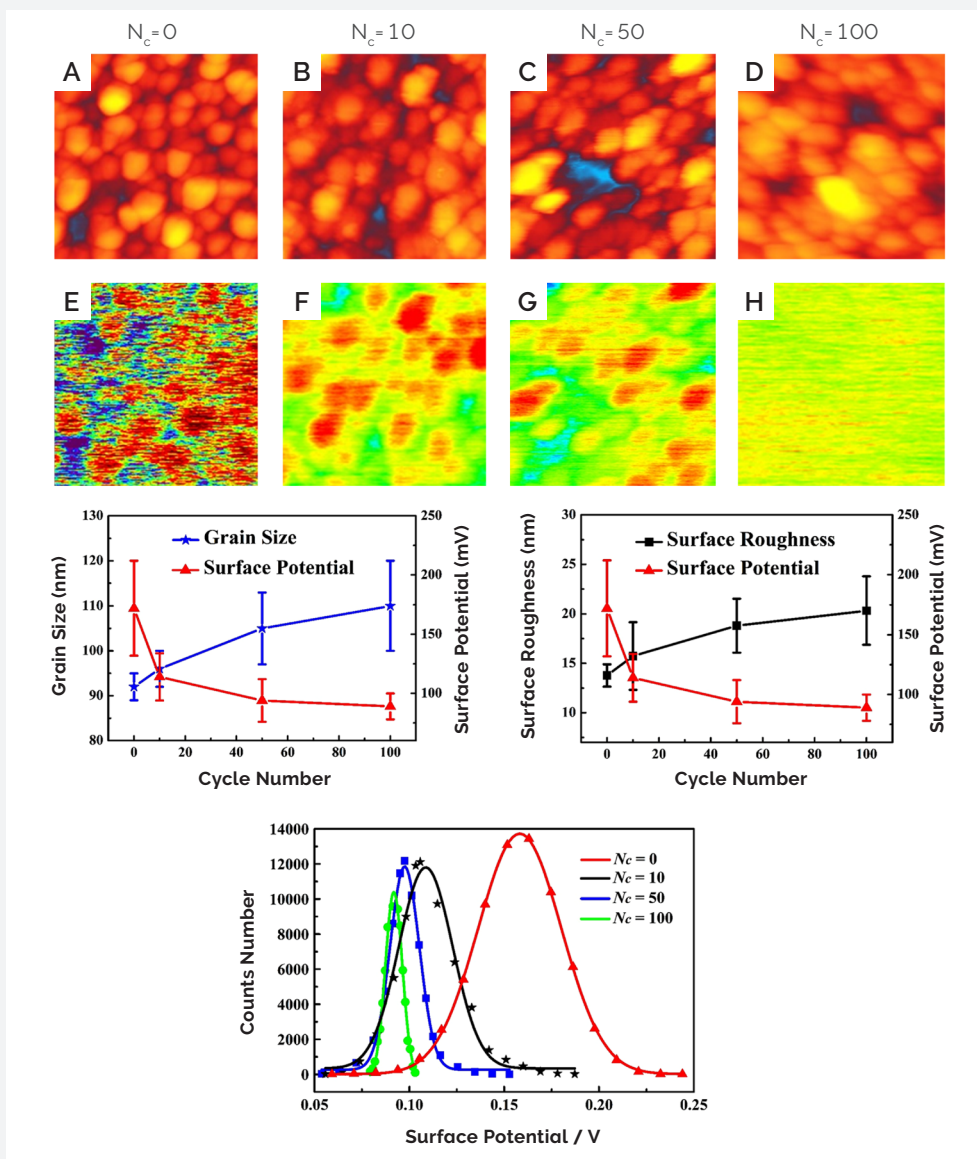


Figure 2: Evolution in surface morphology (A–D) of LCO cathode films, and their surface potential (E–H), measured by KPFM, as a function of the number of charge/discharge cycles. Graphs show similar trend with contact stiffness, where grain size increased linearly while contact potential decreased more dramatically in the first 10 cycles. In addition, the contact potential distribution shows a decrease in variation with the number of cycles.

Lithiation/Delithiation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Anodes

Understanding anode materials with nanoscopic detail can also help improve the overall performance of battery cells. Lithium titanate (LTO) has become a commercially viable alternative to graphite despite having comparatively lower capacity and higher voltage requirements. Advantages include its ability to accommodate three lithium ions in its spinel framework to form $\text{Li}_7\text{Ti}_5\text{O}_{12}$ without volume change, operation within the electrolyte stability window and thus not reliant upon the formation and stability of the SEI, high reversibility, i.e., high coulombic efficiency even at high current rates, ease of synthesis, inexpensiveness, and eco-friendliness.^{6,7}

A major drawback is its low electronic conductivity, which requires engineering (e.g. coating with carbon) to improve performance. However, it is known that $\text{Li}_7\text{Ti}_5\text{O}_{12}$ or the lithiated phase is highly conductive, from spectroscopic and electrochemical studies, and that even a small amount of lithiation can dramatically increase bulk electronic conductivity.⁷ It is thus important to understand how this phase transformation occurs, but because there is no volume change between the two phases, and their lattice parameters are nearly identical, diffraction techniques are unable to physically differentiate them. However, since one phase is insulating, while the other is conducting, current measurements with AFM are ideal to track the nanoscale changes in phase during the lithiation/delithiation process that results in the insulator-to-metal transition.

Fig. 3 shows current maps of LTO overlaid on surface topography, obtained by conductive AFM (CAFM). Note the area scanned is $1\ \mu\text{m} \times 1\ \mu\text{m}$, and the z-scaling is 100 nm. The series of images correspond to points in the electrochemical profile of the first cycle, where the pristine film (A) is first discharged to 50% (B), then discharged to (1.5 V), discharged to 1.0 V, charged to 50%, and finally charged to 2.0 V.

Before cycling, the LTO is completely insulating, as we expect from $\text{Li}_4\text{Ti}_5\text{O}_{12}$. As the LTO is discharged (lithiated), the morphology remains the same, but the average current goes up from $0.12\ \mu\text{A}\ \mu\text{m}^{-2}$, when discharged to 50%, then to $0.58\ \mu\text{A}\ \mu\text{m}^{-2}$, when discharged to 1.5 V. Following total lithiation, i.e., completion of the two-phase reaction, nearly all grains are conducting, as we expect from $\text{Li}_7\text{Ti}_5\text{O}_{12}$. It had been hypothesized that LTO by itself, forms the conductive phase first near the current collector, then evenly propagates upward, towards the interface with the electrolyte. But CAFM measurements show that current is clearly localized within discrete grains and not evenly distributed across the film. This demonstrates that the transition from insulating to conducting phase proceeds instead via a small number of percolation channels between the current collector and the electrolyte.

In addition, when the film is discharged beyond 1.5 V to the LTO cutoff voltage of 1.0 V, current decreased to $0.32\ \mu\text{A}\ \mu\text{m}^{-2}$ and the morphology significantly changes, i.e., the average particle size increased. It is thought that the SEI may have formed, despite the fact that LTO is not known to form the SEI, perhaps from the high surface area of the thin film. Or overlithiation may have occurred at the surface which may form non-conductive species.

Formation of the Solid Electrolyte Interphase (SEI)

The solid electrolyte interphase (SEI) has been the subject of great interest because its formation and stability directly impact battery life, safety, and performance.^{7,8} The SEI is a passivating layer that results from the reduction of the electrolyte on the anode surface. Once formed, further electrolyte decomposition is prevented, stabilizing the electrode/electrolyte interface. The SEI needs to be electrically insulating and impermeable to electrolyte but allow for lithium diffusion, mechanically stable against stress from changes in electrode volume, and insoluble/inert in the electrolyte at the electrode working potentials and temperatures.⁷ A poorly formed SEI can result in

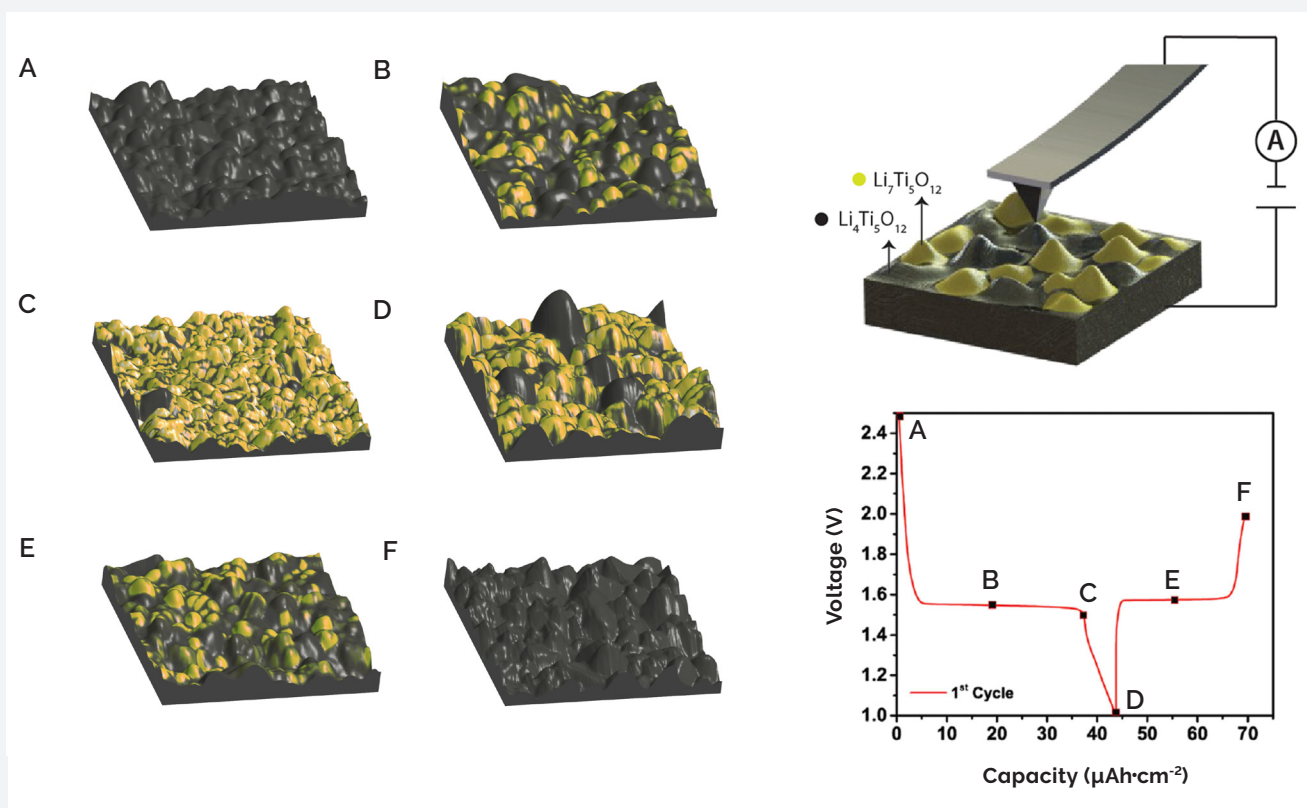


Figure 3: Conductive AFM current maps of LTO anode films overlaid on topography at various states of charge from (a) pristine, (b) discharged 50%, (c) discharged to 1.5 V, (d) discharged to 1.0 V, (e) charged 50%, (f) charged to 2.0 V.

capacity fade and reduction in power density, such that understanding and tuning the SEI formation is critical in improving overall battery performance.

Unlike other measurement techniques that require high vacuum environments, AFMs can be operated under a variety of environmental conditions making it ideal to image within the sample's relevant working environment. In this example, an electrochemical cell was used in order to understand the formation of the SEI on the basal plane of HOPG during electrochemical cycling.⁷ Nucleation and growth of the SEI within a commercial battery grade electrolyte solution (1 M LiPF₆ in 50/50 v/v ethylene carbonate/dimethyl carbonate) could therefore be observed in real-time. In addition, the AFM was also placed inside the glovebox so that measurements could be done in an inert atmosphere as required by the air-sensitive reagents.

Fig. 4 shows the electrochemical cell illustrating how the HOPG electrode can be imaged in situ within the electrolyte solution during electrochemical cycling.

The 15- μm images show the surface topography of the HOPG electrode before and after cycling, and shows the SEI layer forming at the end of the cycle. The series of 4- μm images within the 15- μm images (indicated by

the white box), shows the nucleation and growth of the SEI layer in real time. The image number indicates the position in the voltammogram during the first cycle.

The white arrows in image #4, corresponding to a prominent dip in the voltammogram, indicates nucleation sites of the SEI. At 0.8 V the SEI was detected along the step edges, and at 0.5 V along the basal plane, correlating with the current dip between 0.8-0.3 V. Beyond 0.4 V (image #5), the SEI formed a uniform layer which remained stable until the end of the cycle. Note that after the SEI formed, the morphology remained the same during the second cycle, while the voltammogram showed a much smaller dip between 0.8-0.3V.

This example demonstrates how the AFM can be used to study the complex formation of the SEI under realistic operational conditions, which can be used to understand how they can be engineered to produce the optimal properties for improving battery performance and lifetime.

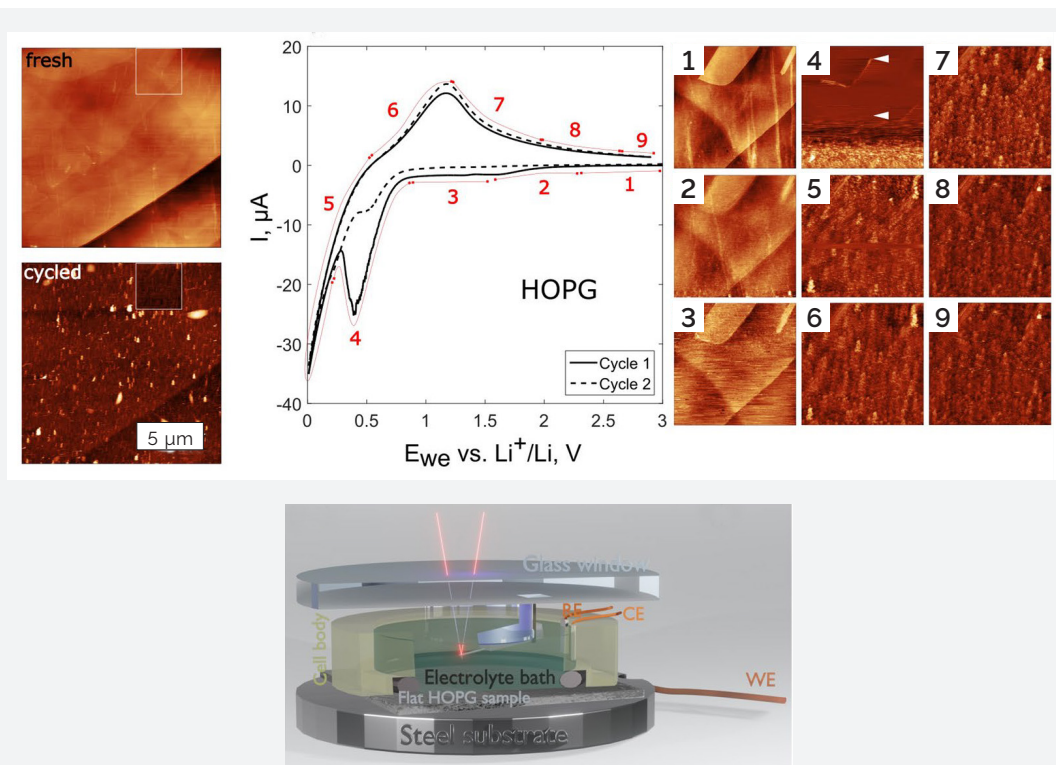


Figure 4: Topographic images of HOPG recorded at different points on the voltammograms during cycling in the presence of 1 M LiPF₆ in 50/50 v/v EC/DMC electrolyte solution and at 2 mV/s cycling rate. The 1-9 series shows changes in a 4 μm section of the 15 μm survey scans (top, left); white arrows indicate locations of SEI nucleation. The bottom is a homebuilt setup for facile in situ measurement of SEI nucleation and growth on different anode substrates.

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