

### Electrochemical high-speed AFM dynamically probes fast-charging battery materials

An ongoing challenge for Li-ion automotive batteries is to be able to recharge them quickly, and thus compete with the refueling times of gasoline vehicles. Such fast-charging rates force battery materials to operate at extreme rates. Historically, such high rates were avoided because they led to accelerated degradation and therefore shorter battery life. However, the new targets demand that batteries operate in this regime. Accordingly, there is a renewed scientific interest in examining the fundamental origins of degradation at these faster rates. Since corresponding degradation events are found to be localized, the macroscopic measurements of voltage, current, and temperature do not provide sufficient insights to understand degradation events. *In situ* or *in operando* imaging is therefore required to study degradation events while they are happening.

These degradation events are chemical changes such as the formation of a new solid phase due to unwanted side reactions, such as Li plating, and simultaneously result in physical changes. Hence,

one can obtain many insights by tracking physical-geometrical evolution during operation. Atomic force microscopy (AFM) is a promising technique to map such geometrical evolution but is constrained by the slower image acquisition times ( $\sim$ min). An additional challenge is to configure AFM for the unique electrochemical environment of operating cells.

Guangyi Shang, Zhuanfang Bi, and colleagues from Beihang University and Singapore University of Technology and Design have advanced AFM to break these constraints and provide meaningful imaging for fast-charging battery materials. The study was recently published in the *Review of Scientific Instruments* (doi:10.1063/5.0024425).

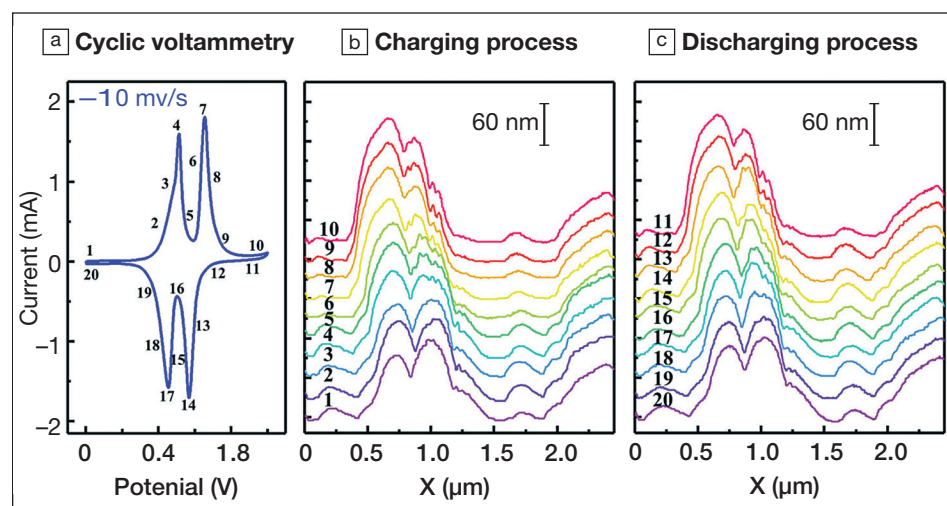
The researchers combined advances in AFM in other scientific disciplines to extend the capabilities of AFM to study electrochemical systems. They borrowed high-speed AFM to improve the image acquisition time from a few minutes to a few seconds. In this setting, a smaller cantilever (i.e., AFM probe) is used since it has a higher resonant frequency, lower spring constant and allows for faster scans. The downside of such a cantilever is its small dimensions. The researchers developed a custom optical detection

system to accurately detect the displacements of the smaller cantilever.

A large image window was achieved using a scan stage that was actuated by two piezoelectric stacks to provide accurate, fast, and independently controlled motions in  $x$ - and  $y$ -coordinates ( $z$ -coordinate is the sample height to be mapped using the AFM). A custom electrochemical housing was also built to support the AFM tip holder, electrolyte, reference, and counter electrodes. The working electrode—the sample of interest—was mounted on the sample stage and moved relative to the electrochemical housing. The electrochemical housing had a glass window at the bottom for laser optics to detect the cantilever displacement. Such clever instrumentation allowed faster image acquisition as well as a larger image window compared to the traditional electrochemical AFM.

Figure a–c shows example scans of  $\text{LiMn}_2\text{O}_4$ —a positive electrode material for Li-ion batteries.  $\text{LiMn}_2\text{O}_4$  particles are  $\sim 300$  nm in size and are spin-coated on a gold foil. During the experiment, these particles are charged and discharged rapidly (in 100 s each) and 10 AFM scans are captured during each operation. The surface topological changes are compared during charging and discharging (see Figure b–c). For clarity, surface evolution along one coordinate axis is shown, while the images capture a  $2.5 \times 2 \mu\text{m}^2$  window at 0.75 frames per second.

While discussing the relevance of this study, Jonathan Larson from Lawrence Berkeley National Laboratory (not related to the study) says, “Without question, the advancement of basic energy-storage science stands to greatly benefit from the development of further creative approaches that can expand nanoscopic characterization capabilities of energy-storage interfaces in their native environment. This is acutely true for techniques that can *simultaneously* access combinations of relevant parameter spaces such as time, space, electrochemical condition, chemical content, electrical



$\text{LiMn}_2\text{O}_4$  is electrochemically charged-discharged (= cyclic voltammetry) and *in situ* atomic force microscope (AFM) scans are carried out simultaneously. (a) The electrochemical scan sweeps 0–1 V in 100 s, that is, at a 10 mV/s scan rate; subsequently, the voltage is swept back to 0 in the next 100 s. Ten AFM scans are taken during (b) charging and (c) discharging. The larger scanning window  $\sim$ micron<sup>2</sup> and smaller acquisition time  $\sim$ 1 s for an electrochemical system are key breakthroughs of the new technique. The numerals in (b) and (c) correspond to voltage states in (a). Credit: Zhuanfang Bi and Guangyi Shang.



properties, pressure, etc.” In his opinion, the group has done a nice job of expanding the electrochemical research community’s characterization toolbox by integrating a handful of these relevant measurement parameters with their recently developed “electrochemical high-speed AFM.” The utility of the new tool to track the nanoscopic structure of electrochemically active material as a function of both time and electrochemical

potential is well conveyed in their article, as well as the video provided in the supplemental material. Larson is curious to see the future work that follows.

The researchers are excited about various future investigations for this technique. Other positive electrode materials such as lithium iron phosphate and lithium nickel manganese cobalt oxide will be studied, particularly over larger voltage windows where they have been known to

undergo morphological changes. Another interesting possibility is to study negative electrode materials like graphite and silicon, which are known to show side reactions and volume expansion. Such *in situ* imaging studies will finally allow researchers to verify degradation predictions of physics-based battery models, especially at faster rates relevant to next-generation batteries.

**Aashutosh Mistry**

### Trigonal prismatic cage molecule enables new type of 3D covalent organic framework

Porous crystalline solids are made up of molecules connected in a network such that there is a high degree of porosity. Think of tinker toys: large, complex node molecules are coordinated to smaller linking molecules, forming two- or three-dimensional (3D) arrays. The chemistry of these molecules allows materials to be rationally designed with specific—even dynamic—structures and functionalities. Covalent organic frameworks (COFs) are a type of porous crystalline solid that, to date, have mostly been realized as stacks of two-dimensional layers. In an article published in a recent issue of the *Journal of the American Chemical Society* (doi:10.1021/jacs.0c07732), researchers at the University of Liverpool, UK, describe their work synthesizing a new dynamic organic cage-based 3D COF.

COFs are a cousin of the more well-studied metal–organic frameworks (MOFs),

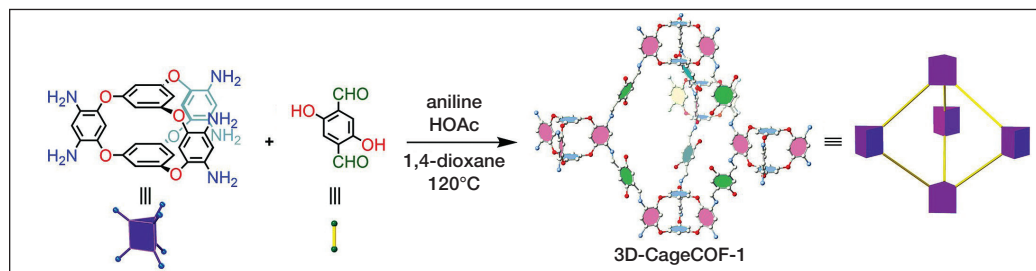
which have a wealth of 3D structures. Researcher Marc Little talks about starting with that family resemblance: “Our approach took inspiration from the three-dimensional secondary building blocks that have been used to synthesize MOFs and enabled the synthesis of topologically diverse MOF nets.” Specifically, molecules with trigonal prismatic coordination greatly expanded the variety of 3D MOF structures, so the researchers worked to design a similar molecule for COFs. They named their bespoke molecule Cage-6-NH<sub>2</sub> for the pendant amine group at each of the triangular prism’s six vertices and the empty cage at its center. Paired with the linear linking molecule 2,5-dihydroxyterephthalaldehyde (DHTPA), Cage-6-NH<sub>2</sub> resulted in 3D-CageCOF-1, the first example of a 3D COF with acs topology, a designation which describes a hexagonal arrangement of linked triangular prisms.

The unique porosity and chemistry of COFs and MOFs allow them to accommodate guest molecules for a variety of purposes. But, according to Little, 3D-CageCOF-1 did this in a surprising

way: “Qiang Zhu, a PhD student working on the project, found that by loading the pores with different solvents, including dimethylformamide, the COF structure changed.” Another PhD student, Xue Wang, built computer models to study the structure of 3D-CageCOF-1. “Using a combination of powder x-ray diffraction and our structural models, we were able to determine that the COF structure expanded to accommodate the solvent molecules in the pores,” Little says. Moreover, this change was reversible. 3D-CageCOF-1 returned to its small-pore phase when the guest molecule was removed via thermal treatment. “Although three-dimensional COFs and MOFs are known to exhibit reversible dynamic behavior, we were surprised to find that our COF switched from a small-pore structure to a large-pore structure as we filled the pores with solvent,” Little says.

With potential for applications in sensing, capture, and catalysis, COFs and their MOF cousins make for a rich and exciting field of research. The Liverpool team is hopeful that further research will build on this work, using the researchers’ approach to synthesize more diverse COF topologies and enable new functionalities. With the trigonal prismatic cage molecule, and its pendant amine groups, 3D-CageCOF-1 takes a big step toward achieving that goal.

**Antonio Cruz**



Scheme for the synthesis of 3D-CageCOF-1 from Cage-6-NH<sub>2</sub> and 2,5-dihydroxyterephthalaldehyde, which can be topologically represented as a triangular prism and a linear strut, respectively. Model atom colors: C, white; N, blue; O, red. H atoms are omitted for clarity. Credit: American Chemical Society.