Lithium whiskers growth and stress generation in an *in situ* atomic force microscope-environmental transmission electron microscope set-up

With the support by the National Natural Science Foundation of China, a research team led by Prof. Huang JianYu (黄建宇), Prof. Tang YongFu (唐永福) and Prof. Zhang LiQiang (张利强) at the Clean Nano Energy Center, State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, reported the first real-time imaging of Li dendrite growth with simultaneous stress-strain measurement by using a novel environmental transmission electron microscopy—atomic force microscopy (ETEM-AFM) platform, which was published in *Nature Nanotechnology* (2020, 15: 94—98).

All-solid-state Li batteries have attracted great attention in recent years due to their potential high energy density and good safety. However, the detrimental Li dendrite growth induced battery failure hinders their commercialization. Resolving the Li dendrite problem in all-solid-state Li batteries requires a fundamental understanding of the electro-chemo-mechanical behavior of Li dendrites. Unfortunately, the basic mechanical properties of Li dendrites remain little known to date, due to several outstanding technical challenges. The fact that Li is chemically very reactive and the dimension of Li dendrite is in nanometer regime precludes any conventional sample preparation, transfer and mechanical property measurement procedures.

In this paper, the authors were able to control the *in situ* growth of Li dendrites with diameter of a few hundred nanometers and simultaneously measure the elastic-plastic properties of individual Li dendrites with and without electrochemical driving forces. The ability to grow and mechanically test the Li dendrites in real time at the nanoscale opens up new opportunities for understanding and resolving the dendrite growth problems in all-solid-state Li batteries.

One breakthrough from this work is the novel use of ETEM that overcomes a long-standing challenge to measure the basic electro-chemo-mechanical properties of the extremely reactive materials such as Li. Inside the gas environment of ETEM, a nanometer-thick Li_2CO_3 forms on the surface of *in situ* grown Li dendrites. Such an ultra-thin Li_2CO_3 layer remarkably stabilizes the reactive Li metal and prevents electron-beam damage, thereby enabling *in situ* imaging and mechanical testing. Thanks to the protection of surface Li_2CO_3 they obtained the first experimental results on the mechanical properties of Li dendrites—the results are unprecedented and unexpected.

The ETEM-AFM platform is innovative since the AFM tip plays a three-fold role: a) serving as a cathode; b) axial confinement to generate growth stress; and c) real-time measurement of growth stress. This platform can be extended to study the science of dendrites in other battery systems such as the sodium, potassium, magnesium and calcium battery systems, and broadly to study the stress-mediated growth of reactive materials at the nanoscale.

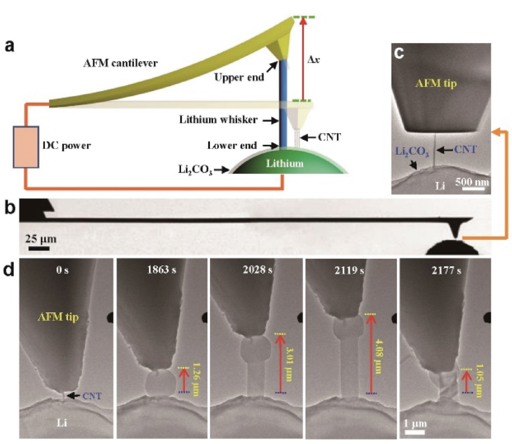

Figure *In situ* ETEM-AFM characterization of stress generation during Li dendrite growth.

The results on the elastic-plastic properties of Li dendrites are extremely important, as they represent the first set of robust experimental data on the previously unknown mechanical behavior of the Li dendrites. The results provide baseline data for verification and validation to a vast amount of theoretical models on the mechanical behavior of Li dendrites with and without electrochemical driving forces.

The results shed light on the material design principles for mitigating Li dendrite growth in all-solid-state Li batteries. It would be impossible to gain such insights without direct measurement of mechanical properties of Li dendrites under electrochemical loading conditions.