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# In Situ TEM Nano Electrochemistry

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Since the inception of the 1st open cell nanobattery study, significant progress has been made in the field of in situ nano electrochemistry. Many new techniques are emerging, which include combing transmission electron microscopy — scanning probe microscopy (TEM-SPM) with environmental TEM (ETEM) to enable metal — gas battery studies; combining TEM-SPM with microelectromechanical system (MEMS) heating devices to enable high temperature battery studies; using large diameter carbon nanotuble as an electrochemical reaction cell to enable in situ liquid cell studies. Our latest results on Li/Na-$O_2$/$CO_2$ batteries, Li/Na-S/Se batteries as well as quantitative measurements of the mechanical properties of Li and Na dendrites will be highlighted [1]. Progress on the in situ studies of solid state batteries will also be presented.

Understanding the mechanical properties of Li dendrite is crucial for developing strategies to mitigate the detrimental dendrite growth problems in all solid-state Li batteries. However, as Li is extremely reactive, measuring the mechanical properties of Li dendrites is very challenging. Using a novel ETEM and atomic force microscopy (ETEM-AFM) device, in situ growth and stress measurement of individual Li dendrites were achieved (Fig. 1). Due to the AFM tip constraint, the growing dendrite under applied overpotentials built up large compressive stresses up to 130 MPa, substantially higher than the stresses previously reported for bulk and micron-sized Li. The measured yield strength of Li dendrite reaches as high as 244 MPa, comparable to that of stainless steel. These results enabled us to establish an overpotential-driven growth map of Li dendrite controlled by its elasto-plastic behavior in the solid electrolyte, thereby offering design insights into the suppression of Li dendrite growth in all-solid-state batteries.

Understanding the structural evolution of the discharge product $Li_2S$ upon operation of Li-S batteries is inadequate and a complete decomposition of $Li_2S$ during charge is difficult to achieve. Whether it is the low electronic conductivity or the low ionic conductivity of $Li_2S$ that inhibits its decomposition is still under debate. In-situ TEM implemented with a MEMS heating device was used to study Li-S batteries at high temperatures (Fig. 2). It is revealed that $Li_2S$ transformed from an amorphous or nanocrystalline to polycrystalline state with proceeding of the electrochemical lithiation at room temperature, and the precipitation of $Li_2S$ was more complete at elevated temperatures than at room temperature. Moreover, decomposition of $Li_2S$ that was difficult to achieve at room temperature became facile at high temperatures. These results indicate that $Li^+$ ion diffusion in $Li_2S$ dominates its reversibility in the solid-state Li-S batteries. This work not only demonstrates the powerful capabilities of combining in-situ TEM with a MEMS heating device to explore the basic science in energy storage materials at high temperatures but also introduces the factor of temperature to boost battery performance.

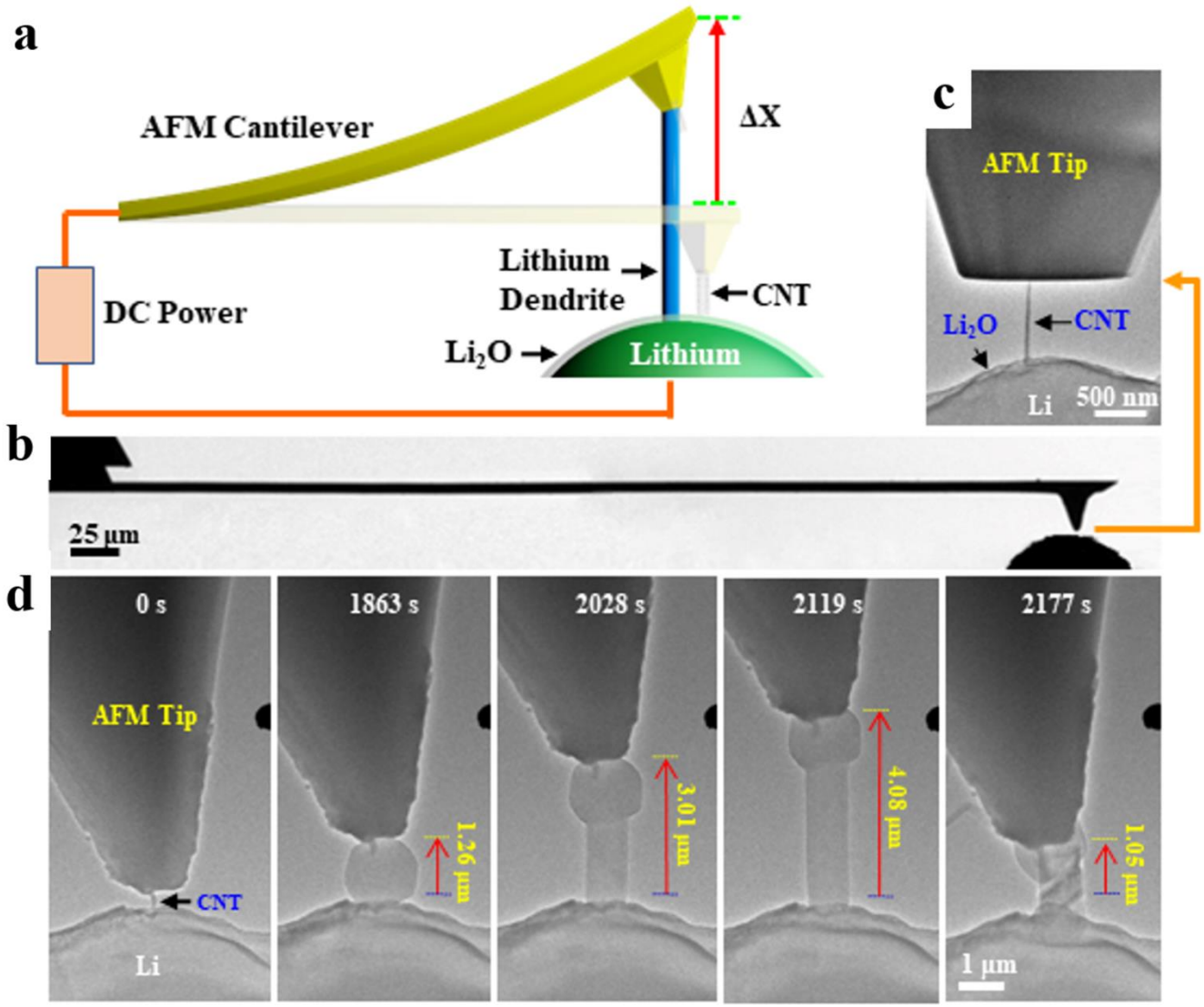


**Figure 1.** In-situ ETEM-AFM characterization of stress generation during Li dendrite growth. (a) Schematic of the ETEM-AFM setup used for imaging and measurement of Li dendrite growth. An arc-discharged CNT was attached to a conducting AFM tip by electron beam deposition of carbonaceous material, and this assembly was used as cathode; the scratched Li metal on the top of a sharp tungsten needle was used as anode, and the naturally formed Li2O on the Li surface as a solid electrolyte. (b) A TEM image showing an AFM cantilever was approaching the counter electrode of Li metal. (c) A TEM image showing a CNT was attached to a flattened AFM tip. (d) Time-lapse TEM images of the Li dendrite growth. A nano-sized Li ball nucleated from the CNT, Li2O and gas triple point (1863 s), which grew with an increase of applied potential. As the Li ball grew to about 1.26 μm in size, the dendrite emerged underneath the ball (2028 s) which pushed the AFM cantilever up, thus generating the axially compressive stress in the dendrite. The spring constant of the silicon AFM cantilever beam is k = 3 N/m in this case. When the dendrite reached 4.08 μm in length, it collapsed (2177 s) due to the axial compression by the AFM tip. The blue dotted line indicates a fixed reference position, and the red arrow indicates the upward displacement of the AFM tip.

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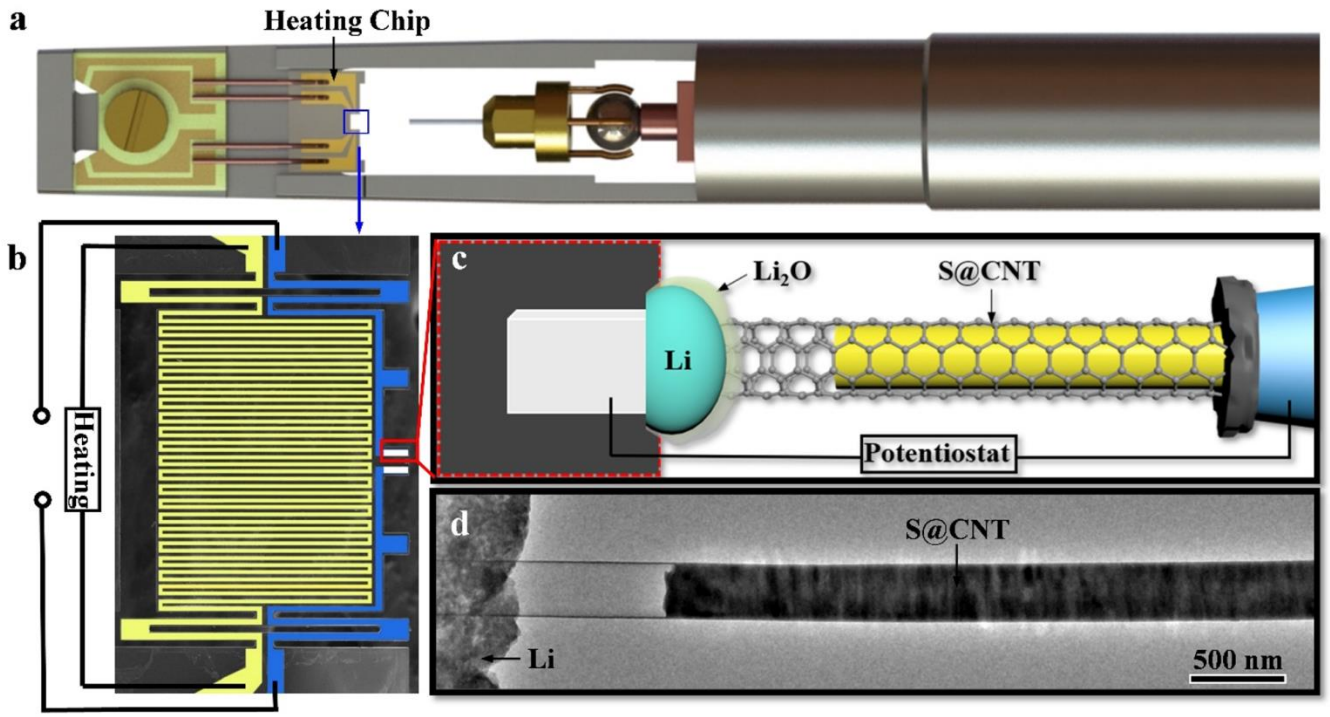


**Figure 2.** A scheme of a TEM sample holder implemented with a MEMS heating device for in-situ TEM high temperature battery studies. (a) A sample holder equipped with the MEMS heating accessory. (b) A MEMS heating chip. (c) Schematic of a Li-S nanobattery. (d) TEM image of a Li-S nanobattery.

## References

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