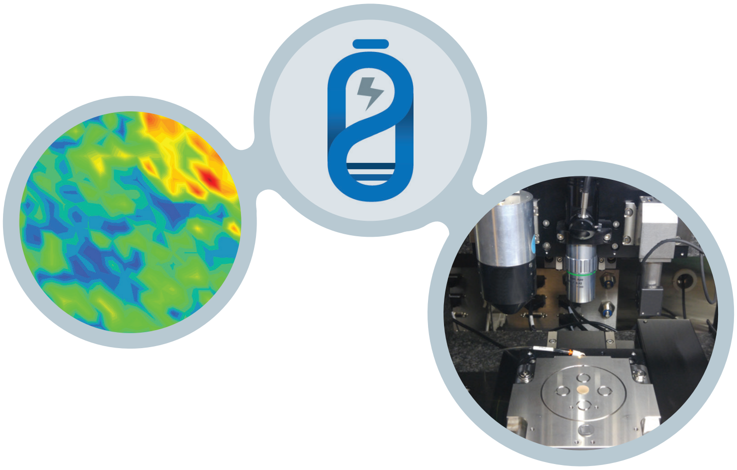

Application Note #1529

Nanomechanical Testing of Battery Materials in Controlled and Inert Environments

Rechargeable batteries have numerous applications that affect our quality of life; smartphones, medical equipment, toys, handheld tools, and electric vehicles to name just a few. Continued development of rechargeable batteries is focused on increasing energy density, the total number of charge-discharge cycles, and safety while decreasing cost and weight. This requires new materials and innovations, such as solid-state batteries, that must undergo rigorous testing before being released into the production cycle. It is this high energy density that can be so dangerous, and is one reason that many devices are prohibited on commercial aircraft. Mechanical damage, including brittle failure of the electrodes and separator penetration, can give rise to dramatic releases of stored energy, including battery fires (Figure 1). Moreover, failures of coatings, mechanical (or ion) induced swelling and stiffening, stresses arising from fabrication, and mechanical stresses and damage from multiple charge-discharge cycles pose significant challenges for new device development and integration. Thus, for both safety and performance reasons, it is necessary to understand how these devices perform mechanically, including each component at the appropriate size scale.

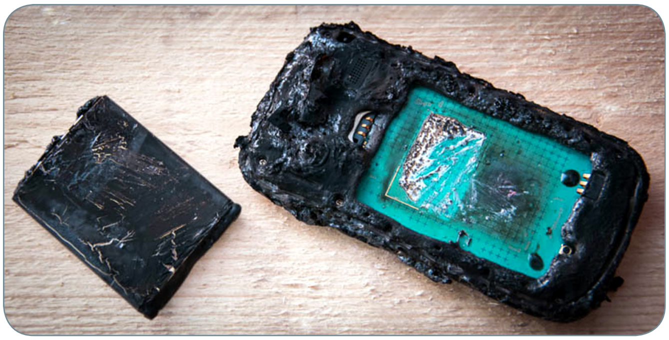

Figure 1. Example of battery failure leading to the rapid release of energy.

Experimental

Lithium is a key component of battery electrodes due to its high electrode potential. However, lithium is highly reactive with water, oxygen, and nitrogen, and will ignite in oxygen when exposed to water or moisture. Thus, testing must be done in a controlled environment. Bruker's Hysitron® TI 980 IO TriboIndenter®, which offers a controlled atmosphere with oxygen and moisture levels less than 1ppm, was used for these experiments (Figure 2).

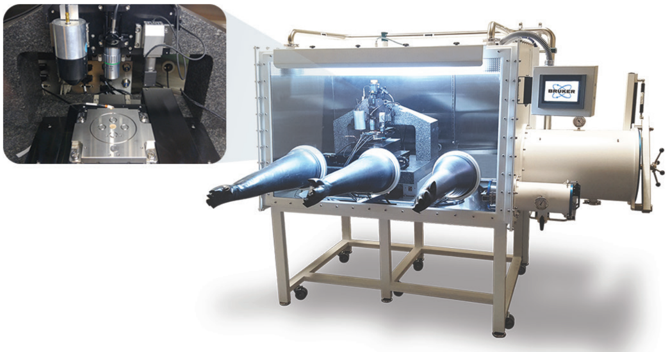

Figure 2. The Hysitron TI 980 IO offers compatibility for most options, including temperature from -80°C to +800°C, indentation at both low (sub 10µN) and high (up to 10N) loads, in a controlled gas environment.

Case A: Time-Dependent Deformation: Creep and Strain Rate Effects for 4N Lithium

Lithium-metal is an attractive material for batteries since it has ultrahigh theoretical specific capacity and the lowest negative electromechanical potential. However, lithium is an extremely soft metal, exhibiting time-dependent plastic deformation.

Determining the nanomechanical properties of battery materials, including elastic modulus, hardness, and understanding nanomechanical behaviors, such as plastic flow of the emerging battery materials, are important for theoretical predictions and failure analysis.

Load-displacement curves were obtained at constant loading strain rate conditions with pure lithium foil using a diamond Berkovich indenter (Figure 3a). Constant strain rate is defined as $\dot{\varepsilon} = \dot{\delta}/\delta$, where ε is the strain, and δ is the depth. However, if the material has constant hardness with respect to depth, this can be simplified as $\dot{\varepsilon} = \dot{P}/P$, where P is the load. Here, the strain rate sensitivity exponent is found to be 0.06, more than twice that of nanocrystalline copper and ten times that of large-grained copper. These indentation measurements, conducted on 99.99% lithium foil, also exhibit visco-plastic on unloading effects, as shown in Figure 3b. This continued plastic deformation, even as the applied load is decreased, provides unique insight into the modes of deformation in these materials.

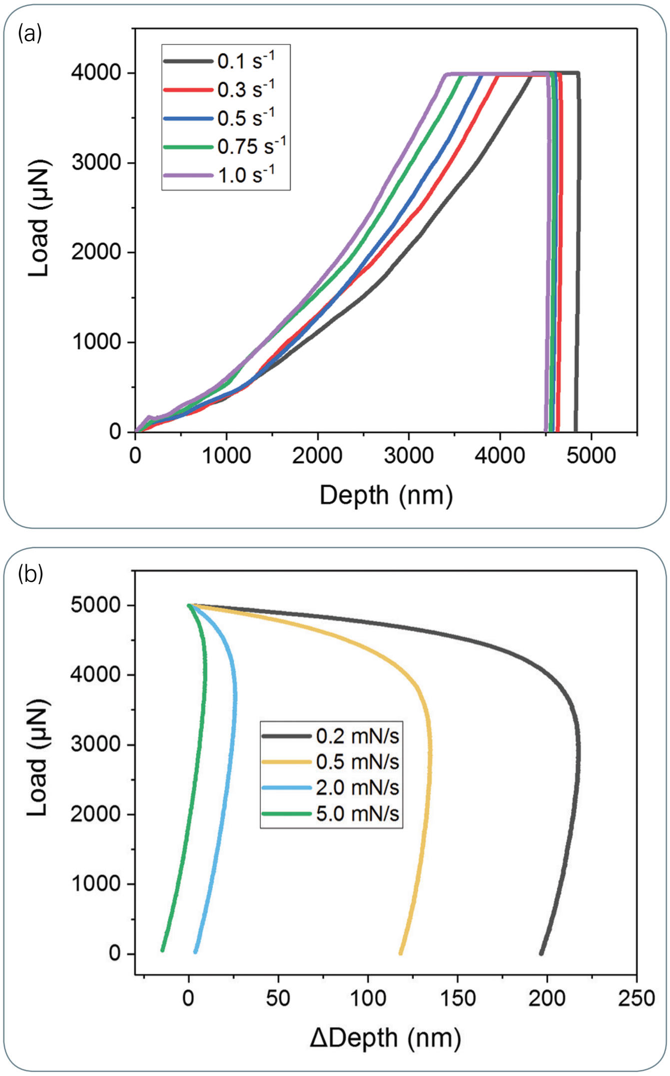

Figure 3. The effect of strain rate of 4N lithium. A strain rate exponent of 0.06 was calculated: (a) The effect of strain rate on the loading curve; (b) Visco-plasticity, resulting in creep on unloading. Even a 1s unload from 5mN results in this continued viscoplasticity. Even more rapid unloading rates, such as -50mN/s, must be applied to use traditional unloading stiffnesses to calculate the reduced modulus.

Case B: High-Speed Mechanical Property Mapping

The materials used for cathodes, anodes, and solid electrolytes are often composites, with microstructural heterogeneity. Mechanical stability plays a critical role preventing degradation of electrodes and solid electrolytes which can lead to the catastrophic failure of batteries [1, 2]. For instance, silicon electrodes can see more than 300% volume expansion during cycling [3]. Thus, investigating mechanical properties, such as the elastic modulus and hardness (strength) of battery materials, is key to understanding the mechanical degradation process of battery materials that occurs during charging and discharging processes.

Maps of modulus and hardness obtained for lithium deposited on a copper working electrode are shown in Figure 4. 625 indents were performed in 30 minutes over an area of 25 x 25µm^2 utilizing Bruker's accelerated property mapping (XPM™) technique. In this case, unloading times of 100ms were used to overcome the viscoplastic effect on the unloading slope. The indentation maps shows the distribution of the hardness and modulus across the sample, Figure 4. This spatial accuracy is due in some part due to the limited indentation depth in comparison to the size of the heterogeneity and film thickness. Figure 5 shows he statistical distribution of hardness and modulus. Assuming various distributions, this data can be analyzed further to determine the average, as well as minimum and maximum, properties of the electrodeposited film.

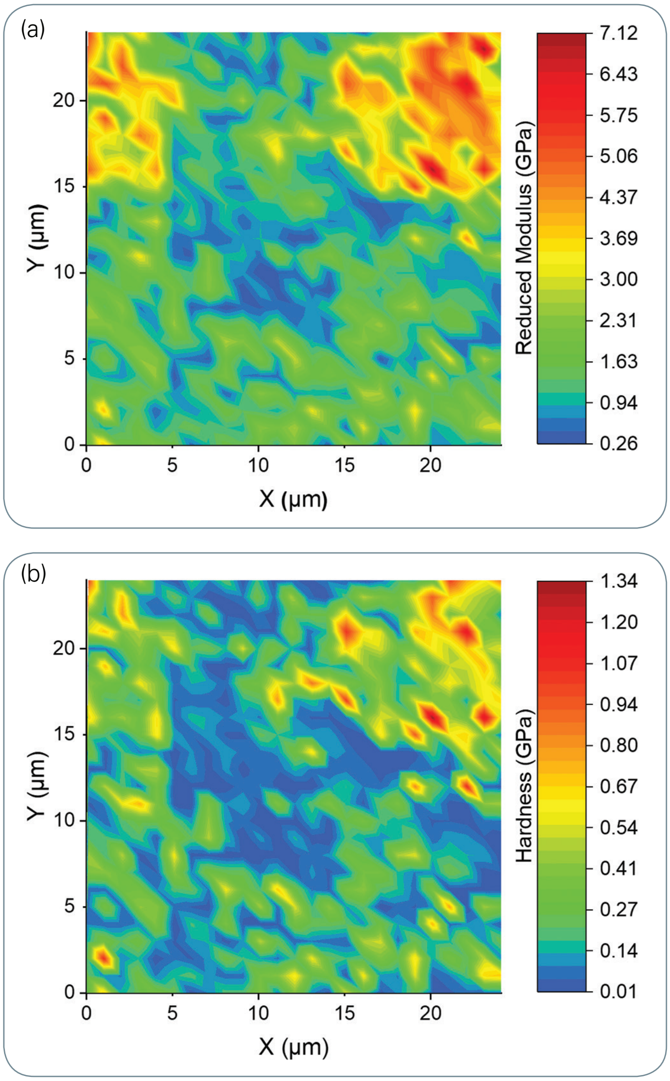

Figure 4. (a) Modulus and (b) hardness map showing variation in the electrodeposited lithium film on the copper working electrode.

Conclusions

Nanomechanical testing of battery materials was performed successfully in a controlled and argon-filled environment utilizing Bruker's Hysitron TI 980 IO testing suite. This preliminary study represents some basic capabilities of the instrument to provide quantitative mechanical characterization for emerging materials and deeper insight for improving mechanical performance.

Acknowledgement

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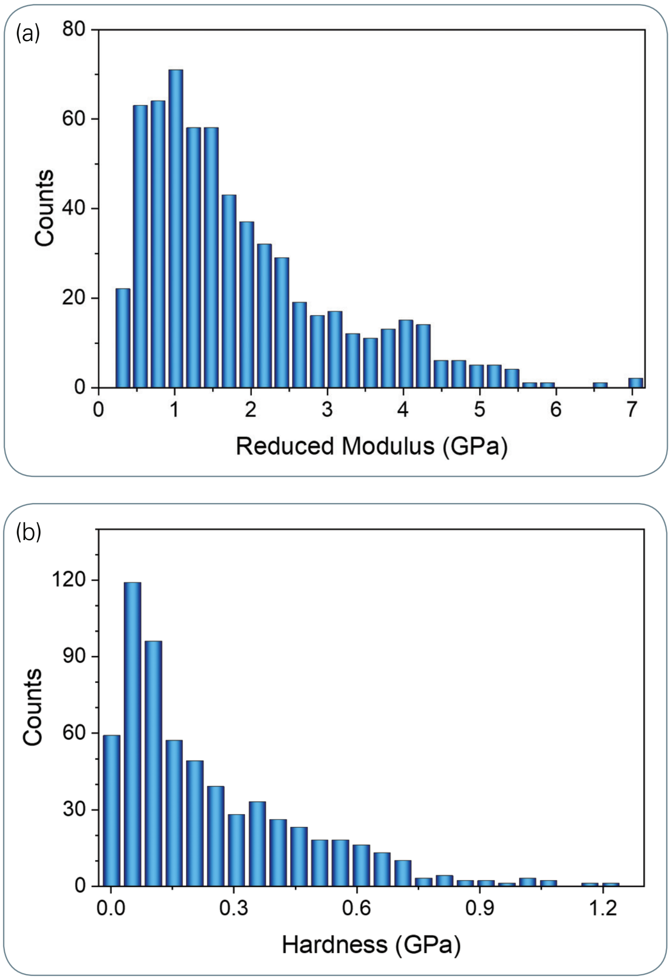

Figure 5. The distribution of (a) reduced modulus and (b) hardness of lithium deposited on copper electrode determined by 625 measurements.

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