Revealing atomic structure and chemistry of sensitive battery materials and interfaces by cryo-TEM

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During regular high-resolution (scanning) transmission electron microscopy (HR(S)TEM) the native state of chemically reactive, mobile and thus strongly beam-sensitive Li-battery materials is hardly preserved. So far, the lateral resolution in TEM is generally limited to low magnifications or low doses, impeding extensive spectroscopic and visual analyses of such materials on the nm or even atomic scale (except for stable compounds). Figure 1a shows a metallic Li dendrite after several attempts to conduct HRTEM imaging in the areas where holes evolved. It is well known that thermally activated processes are slowed down at low temperatures. Consequently, we propose a comprehensive process chain for cryo-TEM of such sensitive materials including the battery disassembly and TEM sample preparation in the inert-gas environment of a glove box in conjunction with cryo-transfer, and the cryo-characterization at LN_2 temperature in the microscope (Figure 1b). The procedure was applied to samples of original battery cells (after disassembly) as well as to test samples with purely Li metal dendrites electrochemically grown on Cu grids. Complementary, Cryo-SEM (with cryo-transfer) was established for characterization on a larger scale. At LN_2 temperature, the mobility and reactivity, both thermally activated, are reduced to such an extend that extensive diffraction-contrast and HRTEM imaging, electron diffraction and even detailed spectroscopic characterization of the same sample region down to the atomic scale becomes practical within periods of a few hours (Figure 1c-e).

Imaging and diffraction revealed the typically single-crystalline nature of Li dendrites with very low densities of extended defects and preferred growth directions of the Li (Figure 1c). Moreover, cryo"TEM allowed for the investigation of the nature and evolution of reaction products and interfaces like the solid electrolyte interlayer (SEI) between the anode and the electrolyte (Figure 1d,e). In particular, the complex morphology of the SEI layer, consisting of different phases and an amorphous carbonaceous matrix could be studied in much more detail. Currently, the applicability of STEM and STEM/EELS are being tested for future characterization on the atomic scale.

In conclusion, cryo-TEM allows researchers to investigate structure formation and degradation of Li-ion batteries, in particular at interfaces, and related materials down to the atomic scale. Hence, it is the basis for prospective development of batteries with enhanced cell lifetime, efficiency and capacity.

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The work is related to another EM study on battery materials, which is being presented at this conference as well: Y. Li, Y. Li, Y. Sun, B. Butz, K. Yan, A.L. Koh, J. Zhao, A. Pei, Y. Cui, Revealing Nanoscale Passivation and Corrosion Mechanisms of Highly Reactive Li Metal by Environmental TEM.

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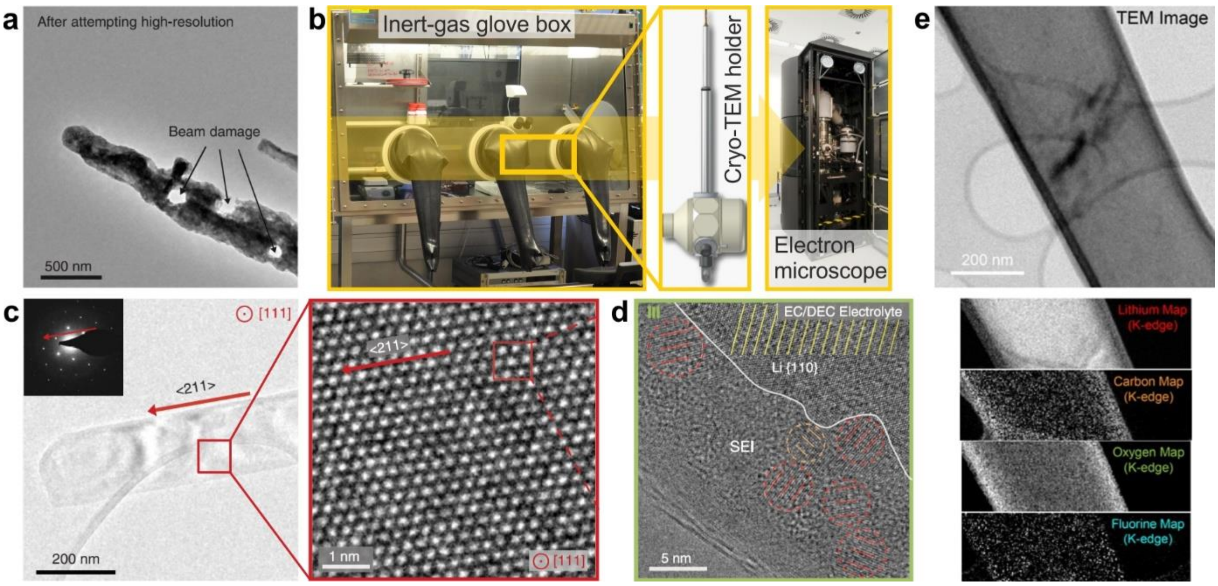

Figure 1: a) Morphology of Li dendrite after (HR)TEM exposure (holes), a) proposed Cryo-TEM procedure to study Li-battery materials: TEM samples are prepared in inert environment and transferred into the microscope, c) Li dendrite with single-crystalline core and SEI layer under cryo conditions allowing for (micro-)structural and chemical analyses down to the atomic scale, d) HRTEM of SEI layer, e) under cryo-conditions, Li dendrites even withstand extensive energy-filtered TEM: element distributions of Li, C, O, F of Li dendrite (same region) without severe e-beam induced sample damage.