

Revealing nanoscale passivation and corrosion mechanisms of highly reactive Li metal by environmental TEM

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Lithium (Li) metal is a high-capacity anode material (3860 mAhg⁻¹) that may enable high-energy batteries for electric vehicles and grid-storage applications. However, pure Li metal is highly reactive and it is repeatedly consumed when exposed to liquid electrolytes (during battery operation) or ambient environment throughout battery manufacturing. To study these corrosion reactions on the nanoscale in the transmission electron microscope (TEM) is difficult due to the high mobility and chemical reactivity of both Li metal and its surface corrosion films. To master the before-mentioned challenges, we in situ generated pure Li metal inside an environmental microscopy (ETEM) by electrodeposition utilizing a Nanofactory STM holder, a Li-coated tungsten tip and a C-coated counter electrode (Figure 1a). Reduced beam-current densities and short expose times allowed for the investigation of the Li evolution in various gas environments by means of ETEM imaging, electron diffraction and even energy-filtered TEM imaging for mapping the light elements Li, O and N during the reactions (Figure 1c).

The systematic ETEM experiments in different environments revealed the nanoscale passivation and corrosion processes of Li metal in pure oxygen (O₂), nitrogen (N₂) and air/water vapor, respectively. Dry O₂ and N₂ generally cause the formation of uniform and dense layers on Li (Figure 1b), where Li nitride, being an excellent Li-ion conductor, appears to be relatively stable even under ambient conditions. However, traces of water cause the formation of highly porous Li hydroxide on the metallic Li (Figure 1c) that allows reactive species (gas or surface diffusion) to penetrate and continuously react with the remaining Li leading to massive corrosion.

To exploit the self-passivation of Li for application, a dry-N₂ pre-treatment of pure Li-metal electrodes is already introduced before the assembly of test batteries in the lab. First results demonstrate that the high ionic conductivity and stable interface of Li nitride results in superior battery performance with dendrite-free cycling and low voltage hysteresis.

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 Reactive Battery Materials in Gas Environments, *Nano Lett.* 17 (2017), 5171 - 5178, DOI: [10.1021/acs.nanolett.7b02630](https://doi.org/10.1021/acs.nanolett.7b02630)

The work is related to another EM study on battery materials, which is being presented at this conference as well: Y. Li, Y. Li, A. Pei, K. Yan, Y. Sun, C.-L. Wu, L.-M. Joubert, R. Chin, A.L. Koh, Y. Yu, J. Perrino, B. Butz, S. Chu, Y. Cui, Revealing atomic structure and chemistry of sensitive battery materials and interfaces by cryo-TEM.

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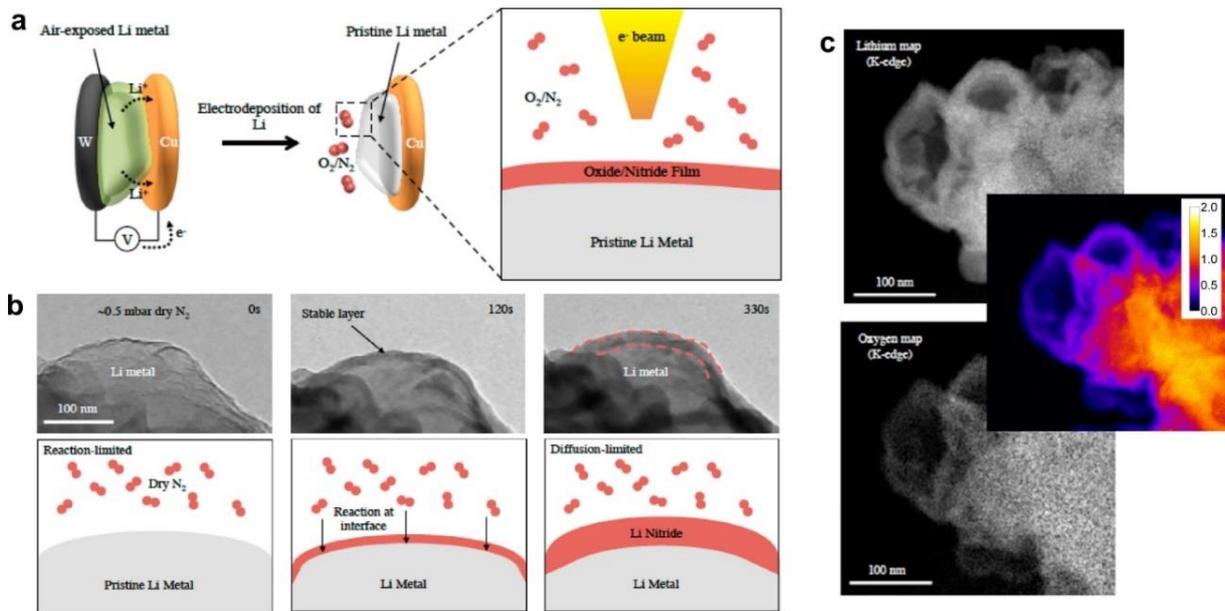


Figure 1: a) Experimental setup for environmental study of pristine (metallic) Li: Nanofactory STM holder with Li-coated W tip used to deposit Li at a counter electrode, b) growth of dense Li nitride passivation layer in oxygen/water-free environment, c) evolution of highly porous Li hydroxide in air facilitating ongoing corrosion of Li metal (structural verification of the hydroxide in publication), the high degree of porosity is reflected in the elemental maps of Li and O as well as in the thickness map.