Cryo-electron microscopy finds place in materials science

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The fast development of electron microscopy has enabled unprecedented achievements in the field of life science and materials science [1–6]. In particular, the 2017 Nobel Prize of chemistry was awarded to three scientists who contributed significantly to developing cryo-electron microscopy (Cryo-EM) [7]. This technique, involving fast freezing the biological samples using liquid nitrogen, was originally designed to keep “live cells” intact from water evaporation and crystallization and immune to electron beam damage to some extent. It has achieved a great success in terms of obtaining high resolution transmission electron microscopy (TEM) images and unveiling several important biological structures [1,2]. In materials science, there are also numerous materials that are sensitive to the electron beam, such as metal organic framework (MOF) materials. To minimize the effect of electron beam irradiation, materials scientists usually lower the operating voltage or electron dose during the TEM experiments [8]. Recently, Zhu *et al.* successfully acquired the atomic structure of a MOF with the help of direct-detection electron-counting camera (Gatan K2 Summit) [6]. However, if materials are also sensitive to ambient conditions, like lithium, which is extremely prone to oxidation, how to address this challenge and secure the atomic structure of intrinsic lithium by TEM? Cui's group from Stanford University offered an excellent example.

The research work just published in *Science* from Cui's team successfully employed cryo-EM, which is widely used in life science, to study the lithium battery [9], a rather hot topic in materials science. To avoid the oxidation of lithium and electron beam damage, they froze the lithium dendrites and solid electrolyte interphase (SEI) layer by using liquid nitrogen and then mounted the sample onto a cryo-TEM holder (Fig. 1a). Their TEM experiments were carried out in a C_s corrected TEM with

Figure 1 (a) Cryo TEM holder with liquid nitrogen. (b) TEM images acquired with Cryo-TEM and standard TEM, and the high resolution TEM images of lithium dendrite (bottom row) [9]. Copyright 2017, American Association for the Advancement of Science.

a spatial resolution of 0.07 nm and the atomic structure of metallic lithium was first revealed by a negative- C_s imaging technique [5]. To their surprise, all of the lithium dendrites are found to be single crystalline (Fig. 1b), which is completely different from previous results that the dendrites are polycrystalline or amorphous (mostly due to oxidation or electron beam damage). Such unexpected findings highlight the critical procedure of freezing samples in order to secure the fresh and intrinsic features of the lithium dendrites. Furthermore, they took advantage of cryo-scanning electron microscopy to examine the facets of the lithium dendrites and suggested

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that the growth directions of the dendrites are governed by the surface energies as most facets they observed are {110} planes with the lowest energy. However, as they also noted, the environment such as the electrolyte would affect the growth directions. In addition, employing the developed approach, the authors studied the effect of different electrolytes on the formation of the beam-sensitive SEI film, which is a crucial layer to ensure a high efficiency of the battery. Interestingly, their results showed that for standard electrolyte, a mosaic structure was observed. While a multilayer structure with ordered SEI was found in a carbonate-based electrolyte with 10 volume % fluoroethylene carbonate. With this new input they suggest that, compared to randomly distributed inorganics in a mosaic structure, the ordered multilayer structure may provide increased mechanical durability.

This study serves as a first example of exploiting the cryo-EM technique to investigate the lithium batteries at atomic resolution after some pioneer attempts in imaging MOF nanocrystals using the same approach [10]. Such technique opens a new window for the atomic-scale investigation of the environment-sensitive materials, which is promising to see novel details that might fail to be unraveled by conventional TEM and will certainly boost the related research in materials science. Right after the publication of Cui's work in *Science*, a similar study of investigating lithium battery using cryo-TEM was reported, where the authors observed amorphous electrochemically deposited lithium and crystalline LiF [11]. As this is a new direction, more and more attention will definitely be attracted to make use of such a powerful technique in materials science to verify its scope of application and in the meantime to address some critical issues, such as, (1) is any phase change involved during the sample freezing for the inorganic materials? (2) are the observed structures and chemical distribution identical as those in dynamic operating conditions? Alternatively, one may utilize inert gases to protect the

environment-sensitive materials (such as using gas cell system in TEM [12,13]) and marry with advanced imaging system (such as Gatan K2 camera [6]) to obtain atomic-scale information of environment-sensitive materials.

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