Low-dose aberration-free imaging of lithium-rich layered cathodes by electron ptychography in the STEM

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It is increasingly accepted that, in order to understand the relationship between structure and function of battery materials, we must know more about their atomic structure. This is particularly important in the technologically relevant lithium-rich transition metal oxide (TMO) cathodes, where the processes that can inhibit their utilization are inherently local [1]. Unfortunately, imaging the complete atomic structure of these materials using electron microscopy is limited by two important factors: the challenge of imaging light elements when close to heavier ones, and the structural changes that can be caused by the electron beam irradiation [2]. In annular dark-field scanning transmission electron microscopy (ADF-STEM), the strong signal from the heavy elements may swamp the signal from the light elements, often rendering the light elements, such as Li or O, invisible. Annular bright field STEM (ABF-STEM) is used to image elements with low atomic numbers but, due to its low efficiency and high sensitivity to precise imaging parameters, comes at the price of potentially significant beam damage. The effect of electron beam under some circumstances resemble the lattice reconstruction and compositional changes induced by the charge-discharge cycles in the Li-rich TMOs, thus hindering the interpretation of results.

Here we show that the emerging technique of electron ptychography can mitigate both these problems. The principle of electron ptychography is that a camera is used to record the intensity in the STEM detector plane for each of the different probe positions in the 2D scan, resulting in a four-dimensional data set from which phase images can be reconstructed [3,4]. This technique offers several advantages compared with the more conventionally used STEM-ADF/ABF. Firstly, heavy and light elements can be visualized simultaneously, and experimentally it is not as demanding on precise optical alignment compared to ABF. It also allows for post-acquisition detection and correction of residual lens aberrations, avoiding the need for final focusing and stigmating which would increase the accumulated electron dose. Finally, much lower beam currents can be used, since effectively all the electrons that reach the detector plane are collected - as opposed to ADF- or ABF-STEM, where only a small fraction of the signal is integrated over a particular angular range. These last two advantages have large repercussions in reducing sample damage.

We have used this technique to image the structure of Li-rich transition metal oxide cathode materials in the pristine, charged and discharged state. The position of the transition metals, Li and O atomic columns can be unambiguously determined (an example is shown in Figure 1). We also show that, by using beam currents in the sub-pA range, beam induced structural rearrangements such as amorphisation or the formation of a surface reconstructed layer can be minimized. This is extremely important to avoid misinterpretation of results, since we can separate beam-induced structural arrangements from those produced by the charging cycles of the material. Furthermore, this approach is widely applicable for other beam-sensitive compounds containing a wide-range of atomic numbers.

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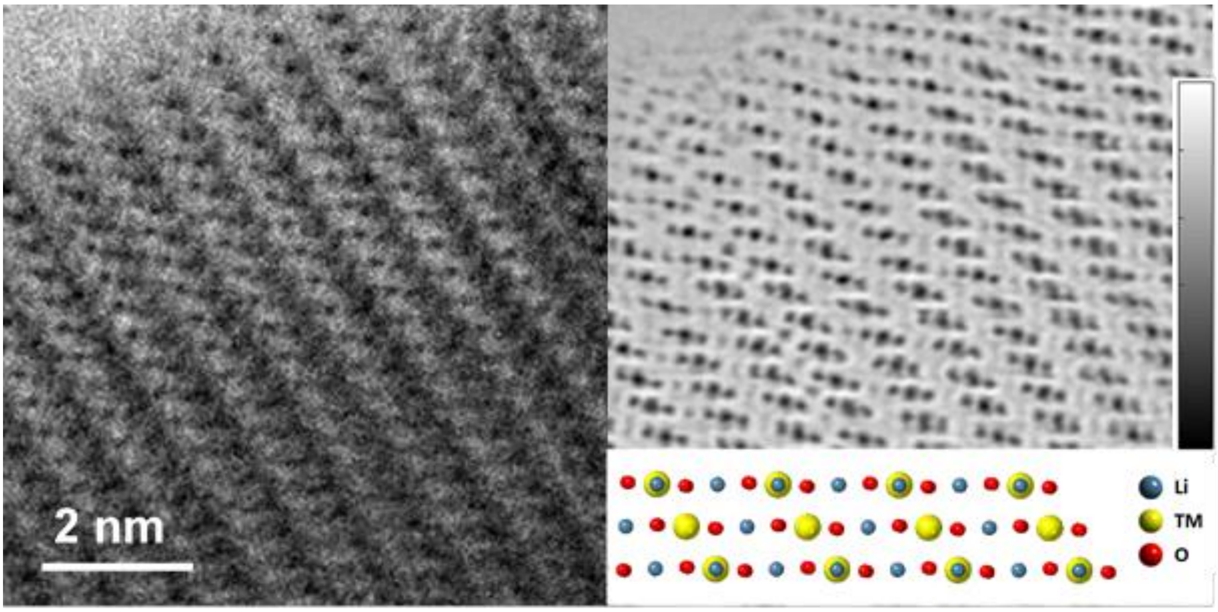

Figure 1. (Left) High resolution STEM-ABF image of charged$Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ viewed along the [010] orientation and (Right) reconstructed phase image of an adjacent area of the same particle. Both images were recorded using a beam current of 0.4 pA. For this beam current, the signal-to-noise ratio in the ABF-STEM image is too poor, while the reconstructed phase image contains the full structural information. Colour bar is 0 to -1.70 mrad.