Direct observation of oxygen lattice distortions in charged lithium-rich layered cathodes by annular bright-field imaging in STEM

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Lithium-rich layered cathodes can accumulate higher energy densities than in conventional layered oxide batteries [1]. The capacity to store charge beyond the accessible oxidation state of the transition metals is ascribed to anionic redox mechanisms during charge compensation [2 - 4]. Despite the importance that anionic reactions have in the charging process, their structural implications remain largely unexplored and not yet understood. Although structural characterization is key to the advancement of large-scale applications, establishing ways of characterising charged materials is currently a challenge. Conventional X-ray and neutron diffraction techniques are often unable to identify local structural rearrangements, or lead to disorder. On the other hand, spectroscopy techniques, like X-ray absorption spectroscopy (XAS), probe local coordination environments, but cannot correlate these with structure modifications directly.

In this work we report on the structural characterization of charged $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ (LNMO) using annular bright-field (ABF) aberration-corrected scanning transmission electron microscopy (STEM). The anion sublattice in LNMO 3*d* transition metal oxide cathodes participates to charge compensation via localisation of electron holes at oxygen sites [4], however structural evidence of this activity has not been reported so far. Using STEM-ABF, the anions network can be imaged alongside the transition metals with atomic resolution. The atomic structure of pristine LNMO viewed under ABF imaging conditions is showed in Figure 1 (a). In the image, darkest spots represent heavy elements. By measuring atom positions with picometre accuracy and precision, combining statistical parameter estimation theory [5] and multi-frame serial acquisition [6], we were able to determine that the oxygen framework distorts after the first charge. Figure 1 (b) shows the histogram of the measured oxygen positions for the charged material. These findings provide an insight into the complex mechanisms that take part in the charge compensation processes, and demonstrate that it is possible to estimate short range structural changes using advanced STEM imaging.

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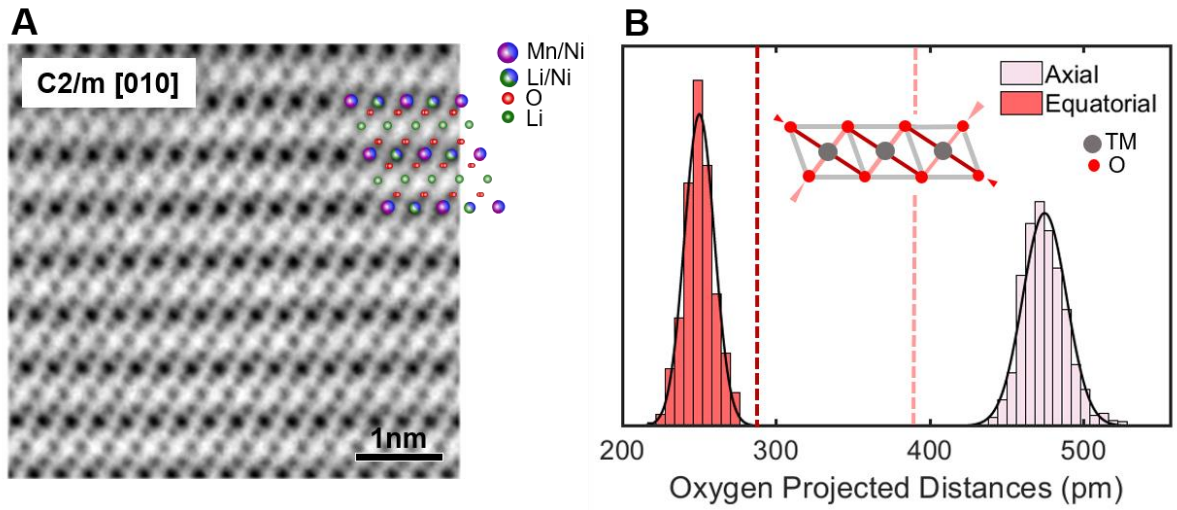

Figure 1. High-resolution STEM-ABF image of pristine $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ viewed along the C2/m [010] zone axis (a). Histograms and fitted Poisson probability density functions of the axial and equatorial O-O bonds in charged LNMO (b). Dashed lines indicate the mean projected interatomic distances for the pristine material.