

## Using Advanced STEM Techniques to Unravel Key Issues in the Development of Next-Generation Nanostructures for Energy Storage

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It is increasingly accepted that, in order to understand the relationship between structure and function of energy storage materials to achieve a much-needed step change in technology development, it is necessary to understand local structure. This is particularly important in the technologically relevant Li-rich transition metal oxides (TMOs), in which the processes that currently inhibit their larger-scale utilization are inherently local. In this class of material, it is known that increasing lithium and manganese contents towards a composition of  $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$  (M is usually Co, Ni, Mn or combinations) leads to much higher capacities [1]. However, these materials suffer from voltage decay on cycling [2], mostly related to structural rearrangement at the atomic scale during charge-discharge cycles. Trapping of metal cations in the interstitial tetrahedral sites or formation of other phases including spinel, rock-salt or  $\text{Mn}_3\text{O}_4$ -like structures have been reported [3,4]. Although there is a general agreement on the structure of the pristine structures [5], the nature, amount and location of different phases formed at various states of charge is still subject of intense debate.

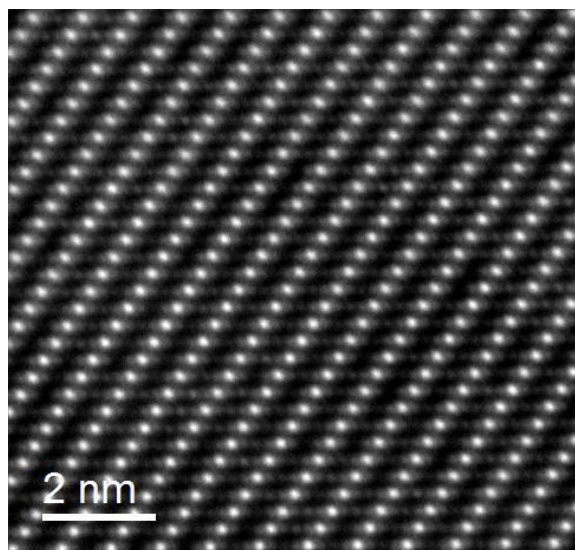
A key structural question in these materials is the origin of the extra capacity and it has been suggested that oxygen loss [6], due to a partial oxidation of the oxygen sublattice is responsible. [7,8]. Recent work has confirmed electron holes on O atoms in Li-rich 3d transition metal oxides using X-ray spectroscopy, XANES and Raman spectroscopy [9]. However, short range structural changes in charged materials still remain poorly understood and requires advanced microscopy to make further improvements in our understanding of these phenomena.

The aim of this work is to show the potential of advanced STEM based techniques to study these materials including imaging the oxygen sublattice. We focus on the case of Li-rich TMOs nanoparticles for use as cathode materials in the next generation of Li-ion batteries. The Li-rich TMO was synthesized using a sol-gel method [10] and the resulting nanoparticles had typical sizes of less than 120 nm. We used aberration-corrected ADF/ABF-STEM combined with multiframe acquisition methods [11] to correct for scan distortions and drift (see an example in Figure 1). This approach provided images with enough quality to monitor the oxygen sublattice for several different compositions.

In addition, the feasibility of using electron ptychography to understand the structure of these oxides was evaluated. This technique recovers quantitative phase data simultaneously with incoherent signals, thus allowing us to image structures that contain light (lithium or sodium) and heavy elements (transition metals) concurrently [12]. Crucially, this method can be performed under extremely low electron doses, which drastically minimises beam damage. Therefore, it enables direct imaging of the atomic structure of pristine and charged samples and the monitoring of structural changes while minimising phase transformations induced by the beam. We will demonstrate that it is possible to obtain high quality atomically resolved data even under electron dose conditions decreased by one order of magnitude.

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**Figure 1:** High-resolution ADF-STEM micrograph of a pristine  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.4}\text{O}_2$  nanoparticle along the  $[010]$  zone axis after drift and scan distortions correction.