doi:10.1017/S1431927622002513
Microsc. Microanal. 28 (Suppl 1), 2022

A Quantitative Understanding of the Short Range Order in Disordered Rocksalt Cathode Materials

Emma Hedley*[1], Liquan Pi[1], Mohsen Danie[2], Weixin Song[1,4], Emanuela Liberti [1,3], Peter G. Bruce[1,4,5,6] and Peter D. Nellist[1]

[1.] Department of Materials, University of Oxford, Oxford, UK
[2.] Electron Physical Sciences Imaging Centre (ePSIC), Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire, UK
[3.] Rosalind Franklin Institute, Harwell Campus, Fermi Avenue, Didcot, UK
[4.] The Faraday Institution, Quad One, Becquerel Avenue, Harwell Campus, Didcot, UK
[5.] Department of Chemistry, University of Oxford, Oxford, UK
[6.] The Henry Royce Institute, Parks Road, Oxford, UK
*Corresponding Author: emma.hedley@materials.ox.ac.uk

Layered cathode materials such as Li-rich NMCs (containing nickel, manganese and cobalt) show promise as new high capacity materials, as the layered structure allows the intercalation and deintercalation of lithium ions during the cycling of the battery. However, these have been slow to commercialise due to issues surrounding voltage hysteresis and capacity fade. Many of the elements currently used in the cathode are expensive and have low natural abundance in the earth's crust but the scope for introducing new more abundant materials is limited by desire to retain the layered structure. Disordered rocksalt materials overcome this issue by having a much larger scope for different elements to be combined, with many examples have shown good performance using only more abundant transition metals such as manganese and titanium [1, 2].

Many of the issues in the cathode are related to structural changes which occur during cycling; several studies have indicated a phase transition from layered to spinel and through to a rocksalt like structure [3]. One perceived advantage of the disordered rocksalts is that by starting with a rocksalt like structure that structural changes on cycling can be avoided. Disordered rocksalts, such as LiMnO2, are therfore proposed as a solution to overcome structural changes in layered cathodes but these also suffer from a gradual capacity fade [2].

Disordered rocksalts consist of a rocksalt structure with an anion lattice of oxygen - often partially replaced with fluorine – and a cation lattice of lithium and one or more transition metals which is primarily disordered. There have been many reports on the importance of short range order within the cation lattice on the percolation network which governs the Li-ion transport; however, despite this the length scale and nature of the ordering is not well understood [1, 4]. The presence of short range order has been shown by diffuse scattering in electron diffraction, peak broadening in x-ray diffraction and pair distribution function analysis from X-ray scattering, but very little quantitative information is currently understood about its nature [4].

In this study we aim to provide a quantitative and localised insight into the nature of the short-range order present within the cation lattice of $LiMnO_2$. We make use of a range of scanning transmission electron microscopy (STEM) techniques such as annular dark field (ADF) imaging and nanobeam electron diffraction (NBED).

We have also used NBED to investigate the changes in the short-range order due to cycling. We have acquired NBED data on the pristine samples and on other samples cycled up to 100 times. This study has shown pronounced changes in the electron diffraction pattern in the cycled material in comparison to the pristine. Figure 2 shows the new peak appearing at a lower angle than the 111 peak of the rocksalt lattice after just 1 cycle and further changes after 8 cycles.

We will combine the information from both of these studies, using standard STEM methods and 4D-STEM to answer the questions surrounding how short-range order in disordered rocksalt cathodes influences the percolation network of Li-ions and hence why these materials show significant capacity changes on cycling [5].

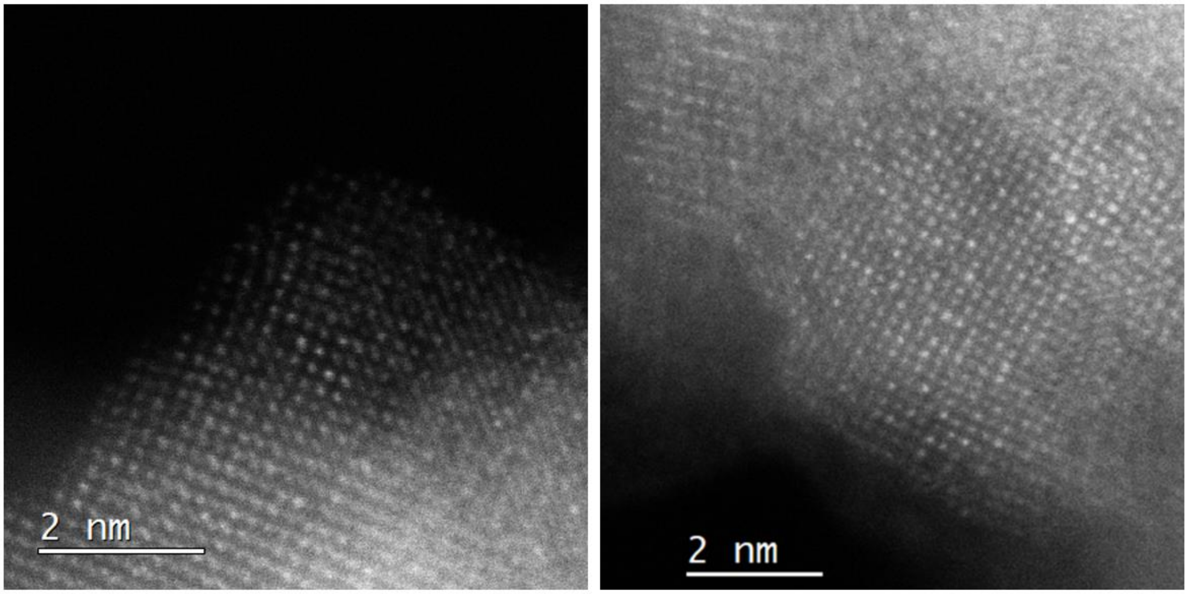

Figure 1. Examples of ADF images of $LiMnO_2$ showing variations in the column intensity due to the presence of transition metals and lithium on the cation sites.

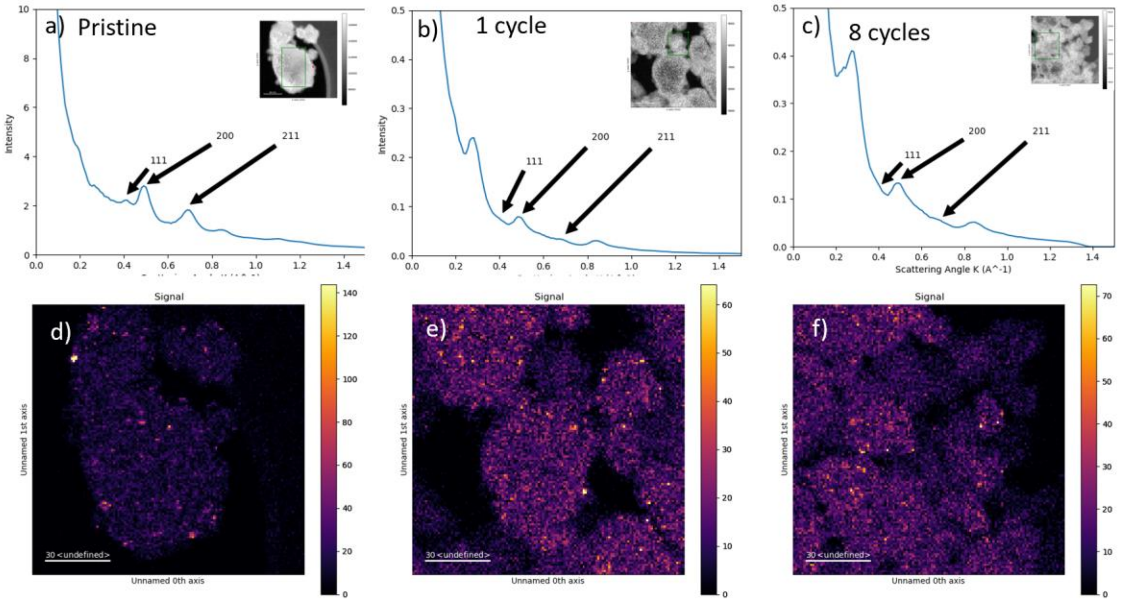

Figure 2. (a-c) Azimuthal integration profiles of the a) pristine LiMnO2, b) after 1 cycle and c) 8 cycles. Insets show the area where the azimuthal integration profiles are generated from. (f-g) Show virtual dark-field images which show the small crystallites which make up the bulk particles.

References:

[1] Ji, H. et al., Nat. Commun. **10** (2019).
[2] Sato, T et al., J. Mater. Chem. A **6** (2018), p. 13943.
[3] Liu, H. et al., Phys. Chem. Chem. Phys. **18** (2016), 29064.
[4] Kan, W. H. et al., Chem **4** (2018), p. 2108.

[5] The authors acknowledge use of characterization facilities within the David Cockayne Centre for Electron Microscopy, Department of Materials, University of Oxford and in particular the Faraday Institution (FIRG007, FIRG008), the EPSRC (EP/K040375/1 "South of England Analytical Electron Microscope") and additional instrument provision from the Henry Royce Institute (Grant reference EP/R010145/1).