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New Insights of Structural Evolution of $LiNi_{0.5}Mn_{1.5}O_4$ Cathode Material revealed by Low Temperature STEM

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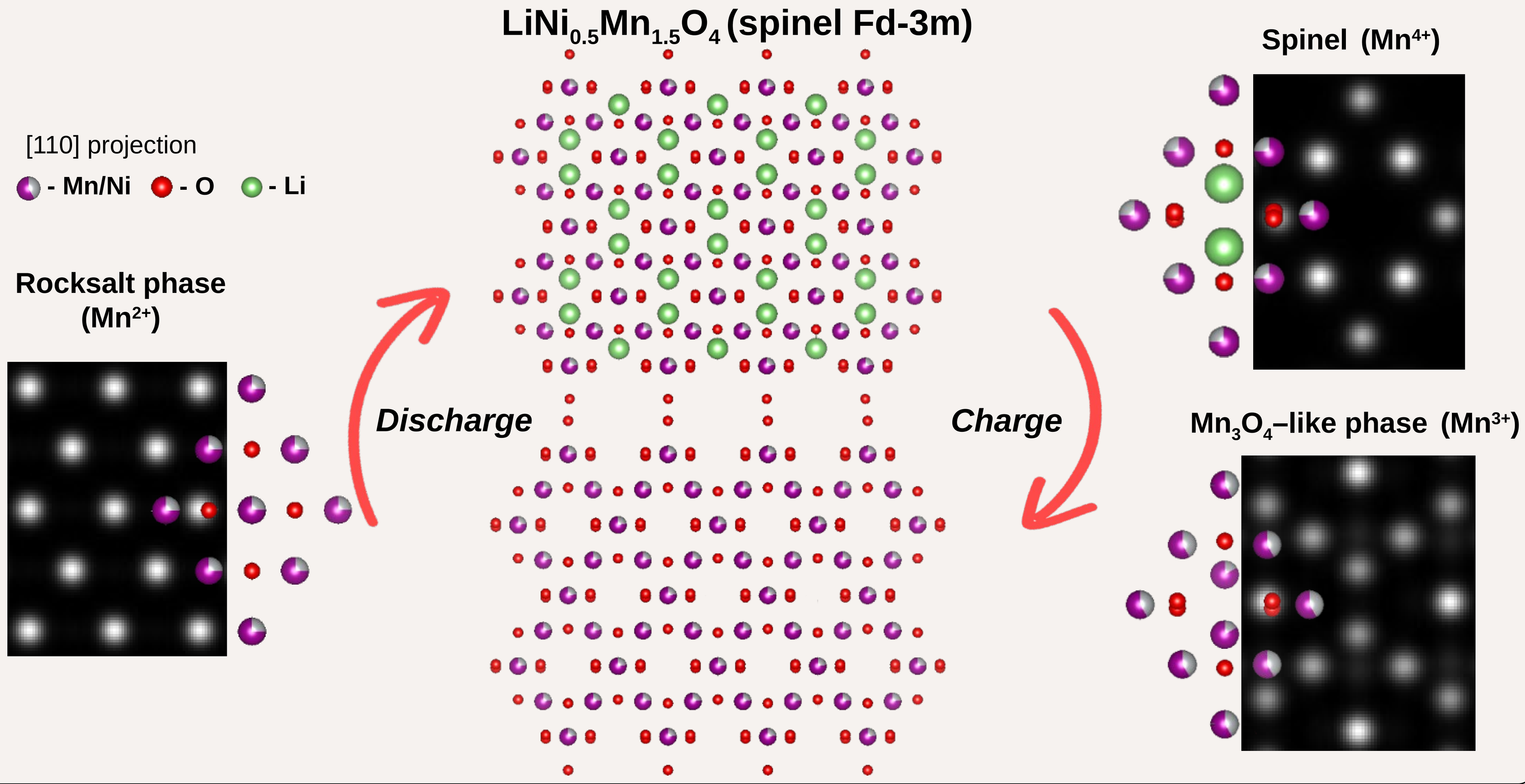
Introduction

$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) is a promising cathode material for application in new generation of high voltage lithium-ion batteries. Various factors such as oxidation state, atomic coordination of Mn and Ni cations, morphology of the particles influence its performance as a cathode material [1], [2].

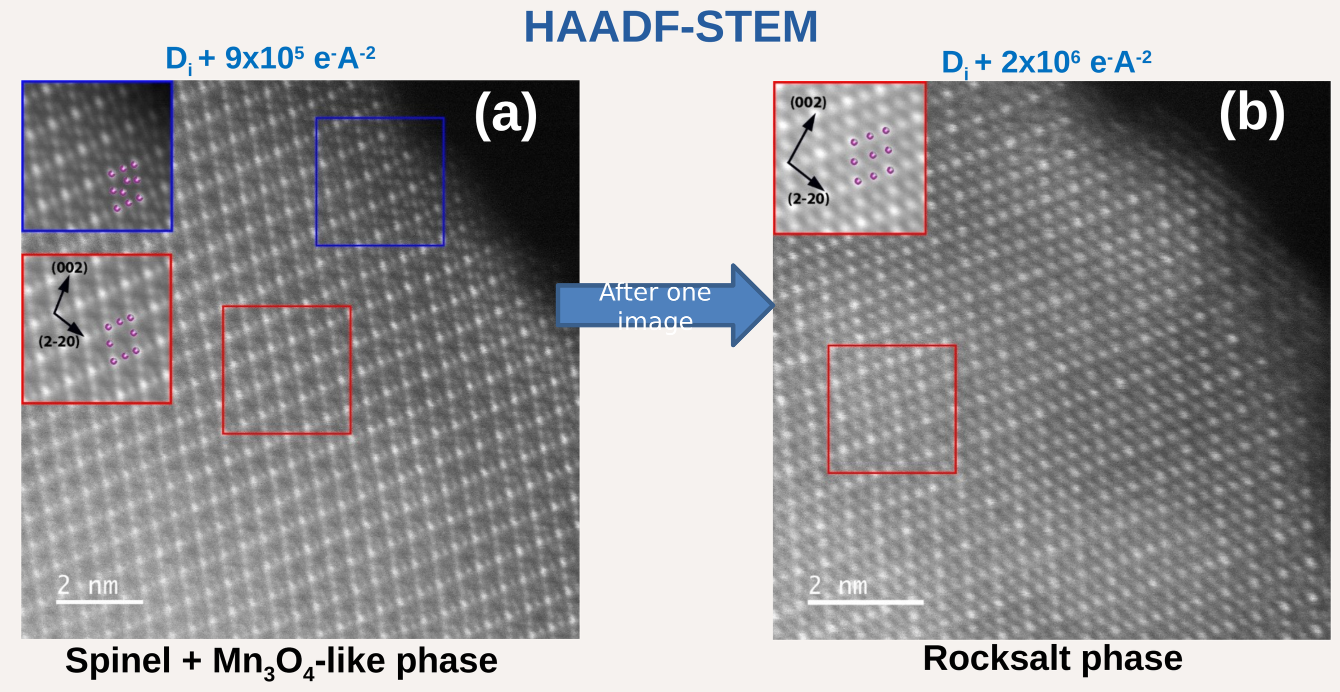
Previous HAADF-STEM investigations showed the formation of rock-salt and Mn_3O_4-like phases after the first charge cycle [3]. However, the spinel-to-rocksalt phase transformation in $LiMn_2O_4$ (LMO) can be induced by electron beam irradiation [4].

Hence, we investigate the effect of the electron beam irradiation on LNMO in order to understand the structural changes due by electrochemical cycling, by excluding electron beam effect.



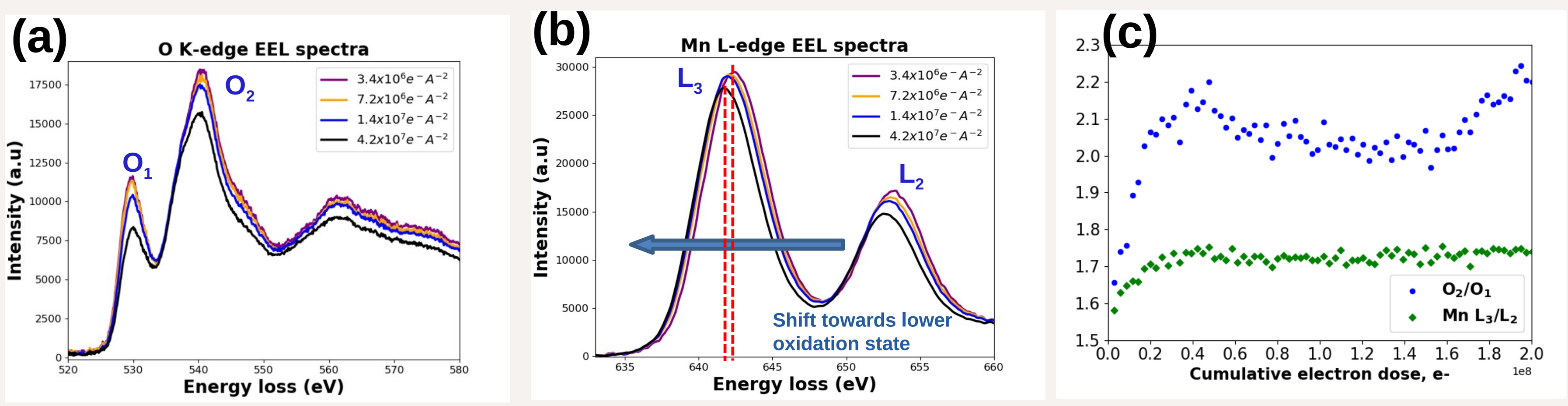
LNMO as-synthesized (RT)

HAADF-STEM



HAADF-STEM consecutive images of the as-synthesized LNMO acquired at room-T: (a) - first image acquired with e-dose $D_i + 9x10^5\ e^-A^{-2}$, **(b)** – second image taken consecutively to (a) with corresponding total e-dose $D_i + 2x10^6\ e^-A^{-2}$ (where D_i correspond to the e-dose needed to align particle into zone axis). On the first image (a) two crystallographic structures are present in the imaged area: mainly spinel phase, and Mn_3O_4-like phase on the 2-4 nm surface (blue area). On the second image (b), the rocksalt structure is present through the same imaging area.

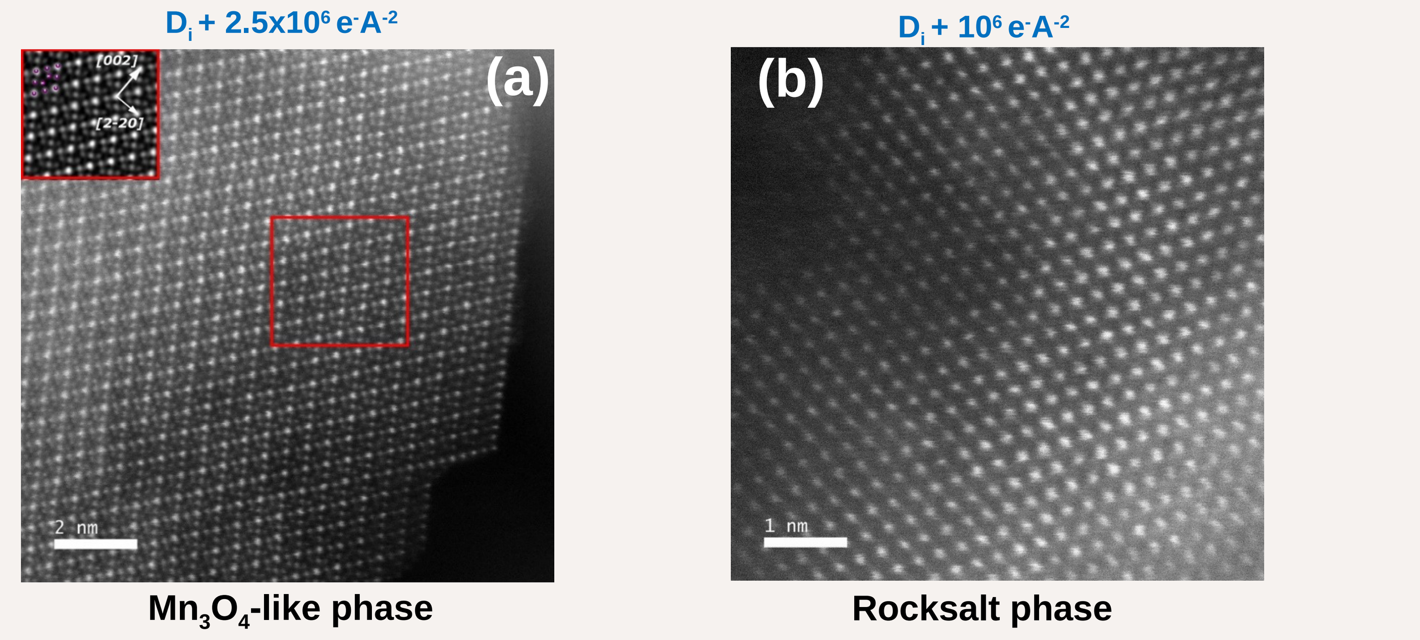
EELS study



(a) - O-K edge and (b) - Mn L-edge spectra extracted from EELS time-series at different cumulative electron doses. With e-dose increasing shape of O and Mn edges change: pre-peak of O decreasing, position of Mn L-edge shifts towards lower energy losses, indicating decrease of oxidation state. **(c) -** Graph shows relative changes of O_2 to O_1, and Mn L_3 to L_2 ratios with electron exposure.

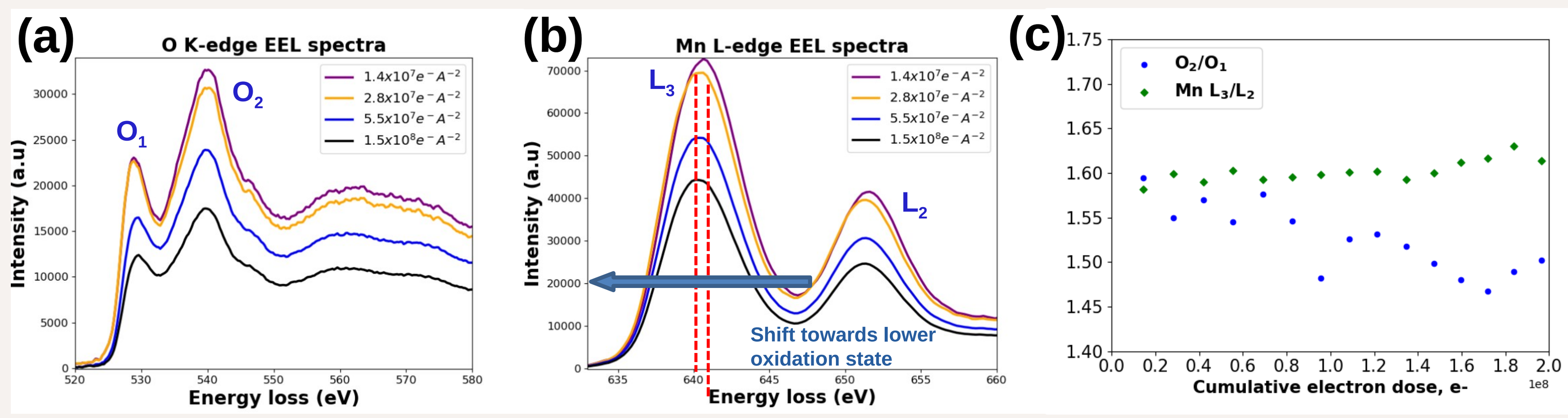
LNMO charged (RT)

HAADF-STEM



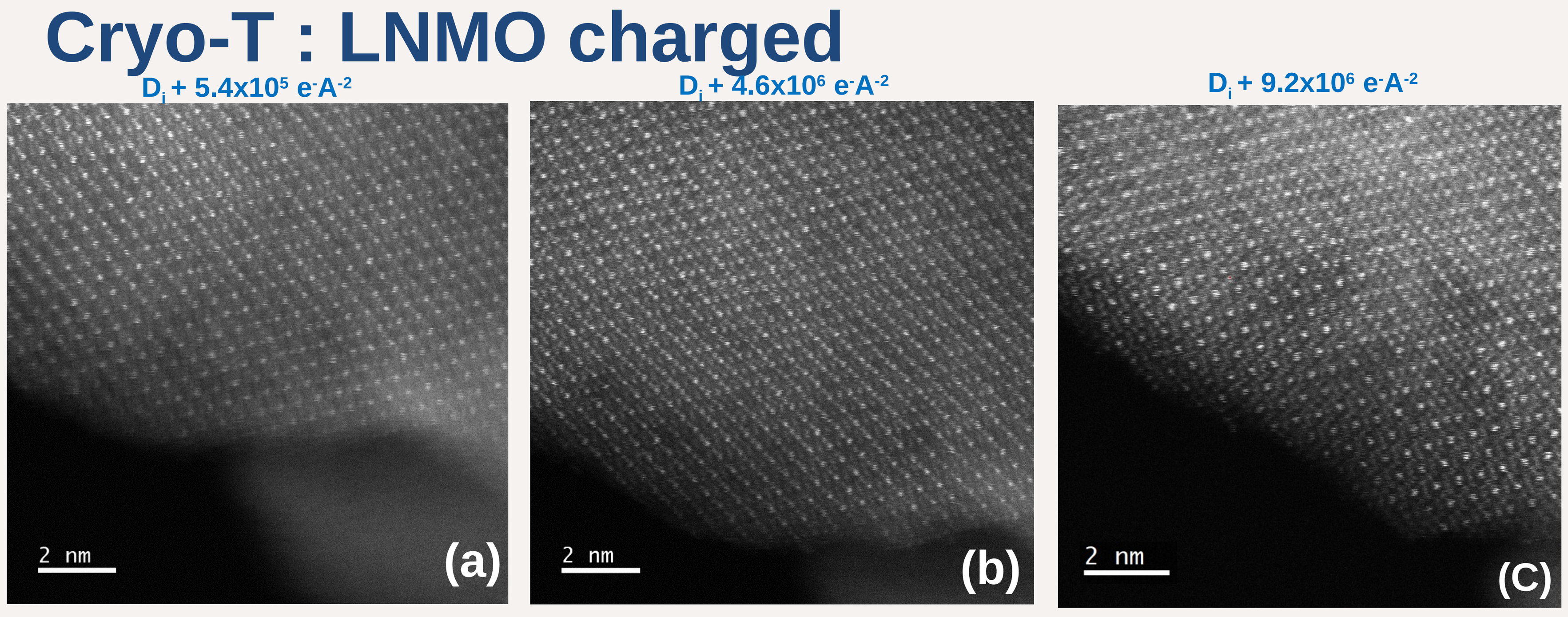
HAADF-STEM micrographs of charged (delithiated) LNMO acquired at room-T. For the sample, two phases can be found: **(a)** - pure Mn_3O_4-like phase, and **(b)** – pure rock-salt phase.

EELS study

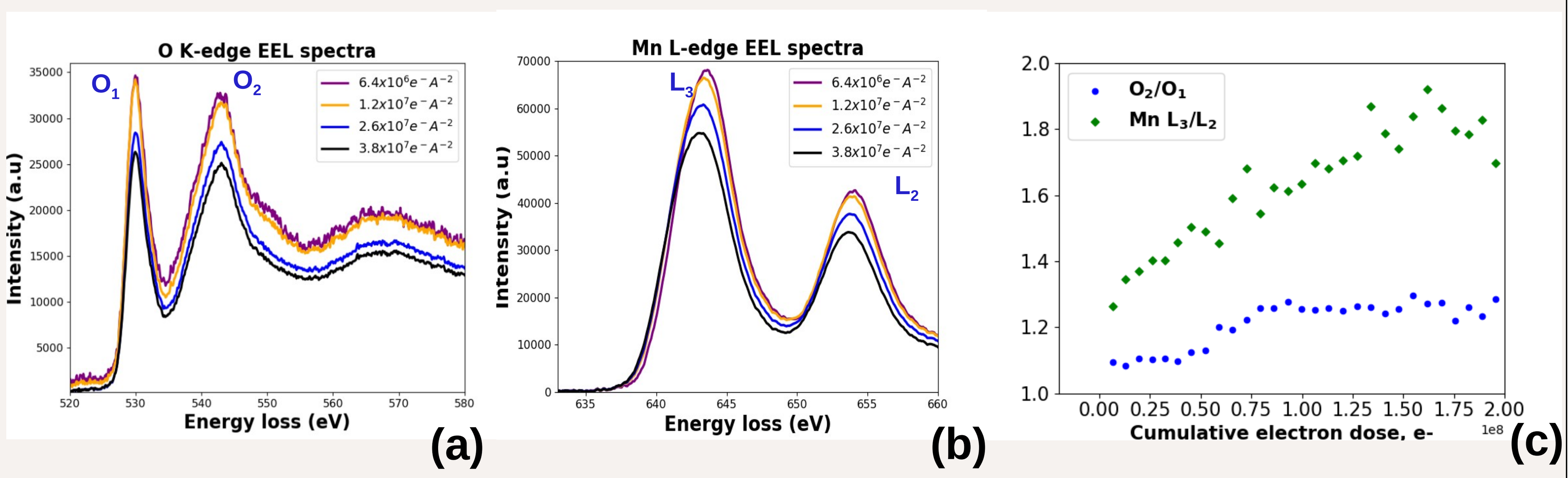


(a) - O-K edge and (b) - Mn L-edge spectra extracted from EELS time-series at different cumulative electron doses. With e-dose increasing shape of O and Mn edges change: overall intensity of O edge decreasing , position of Mn L-edge shifts towards lower energy losses. **(c) -** Graph shows relative changes of O_2 to O_1, and Mn L_3 to L_2 ratios with electron exposure.

Cryo-T : LNMO charged



HAADF-STEM consecutive images of charged (delithiated) LNMO acquired at cryo-T: (a) - first image acquired with e-dose $D_i + 5.4x10^5\ e^-A^{-2}$, **(b)** – second image taken consecutively to (a) with corresponding total e-dose $D_i + 4.6x10^6\ e^-A^{-2}$. On both images only spinel phase present. **(c) -** Transformation of the structure occurs only after $D_i + 9.2x10^6\ e^-A^{-2}$ exposure to the beam.



(a) - O-K edge and (b) - Mn L-edge spectra extracted from EELS time-series at different cumulative electron doses, at cryo-T. Shape of O K-edge is different compare to results acquired for the sample of room-T: the intensity of O pre-peak is higher than the intensity of main peak O_2. Even though Mn L edge also change at cryo-T, the position of L_3 and L_2 lines is different (~644eV for L_3) and L_3/L_2 ratio is smaller compare to room-T data (c).

Conclusions

In this work HRSTEM study reveal sensitivity of LNMO battery cathode material to electron beam irradiation. In particular, rocksalt and Mn_3O_4 – like phases are found to be formed due to the electron beam exposure during imaging. In order to overcome the problem of degradation and to reveal actual structure of LNMO caused by cycling, STEM investigations at Cryo-T has been done and prove to delay electron beam degradation. STEM characterizations at low temperature allow to follow structural and chemical changes due to the cycling and separate them from the beam induced transformations.

References

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[3] - Lin, M. *et al. Chem. Mater.* **27**, 292–303 (2015).
[4] - Gao, P. *et al. Chem. Mater.* **29,** 1006–1013 (2017)