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Cryo-STEM and EEL spectroscopy study of sensitive energy materials

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Interaction of electron-beam with matter generates various signals which provide important structural and chemical information about the material under investigation. At the same time, high energy electron-beam, as a result of radiation damage, can affect intrinsic structure of the specimen. If electron-beam effect is not carefully addressed, this transformation could be mistaken as ones caused by physical process under study. Thus, in order to gain relevant information about the material, mitigation of the beam damage is crucial. In this study, the effect of electron-beam induced degradation is addressed for two energy materials: $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) used as a cathode in lithium-ion batteries and $ZnCo_{1.8}Ni_{0.2}O_4$ (ZCNO) used as a catalyst for oxygen evolution reaction (OER). Both materials were found to be beam sensitive and transform from spinel into rocksalt phase during high-angle annular dark-field (HAADF) atomic resolution scanning transmission electron microscopy (STEM) imaging at room temperature. Here we demonstrate that implementation of STEM studies at cryogenic temperature helps to delay degradation caused by radiation damage, allowing to study native structures of the samples. Cryogenic-STEM investigations were done using double-tilt, cryo-temperature HennyZ holder, that recently become available [1].

During room temperature HAADF-STEM imaging, two phases can be observed for as-synthesized ZCNO: spinel and rocksalt phases on the surface that evolve with continuous beam irradiation (Fig. 1 a-c). Initially (Fig. 1a), there is small amount of rocksalt phase on the surface (separated by the orange line from the spinel phase). After being exposed to 1.5×10^{6} $e^{-}Å^{-2}$ (Fig. 1c), the amount of rocksalt phase significantly increased. In contrast, when imaging is done at cryo-temperature, transformation from spinel to rocksalt phase was not observed under a total electron dose at least four times higher than the dose needed to cause such transformation at room temperature (Fig. 1 d-f). Further studies of ZCNO sample after 1000 ex-situ OER cycles were done at cryo-temperature to decrease the effect of electron beam. It was found that OER cycling cause formation of the shell around the particles, which were mainly not present on the pristine material. Following study is focused on understanding of formation of the shell and its correlation with electrochemical properties.

Similar problem of electron-beam induced degradation was also observed for LNMO cathode material. We found that phases previously reported for LNMO, via HAADF-STEM studies as a result of charging/discharging of a battery cell (Mn_3O_4-like and rocksalt phase) [2], can be induced by the electron beam. Figures 2 (a-b) show such a transformation from spinel into Mn_3O_4-like phase during room temperature STEM imaging for the first charged (delithiated) LNMO sample. After alignment in the zone axis, two phases are present on the particle: spinel phase mainly and Mn_3O_4-like phase on the surface (Fig. 1a). After electron beam irradiation of $1.9x10^6$ e^- $Å^{-2}$, full transformation of the structure into Mn_3O_4-like phase can be seen (Fig. 1b). In addition, formation of rocksalt phase can be also observed after $6.9x10^6$ $e^-Å^{-2}$ total dose exposure (Fig. 1d). However, when the same sample was studied at cryo-temperature, beam-induced degradation happened at higher imaging electron doses (Fig. 2 e-h). Initially there is only spinel phase present (Fig. 2 e-f). Formation of Mn_3O_4-like phase was observed at $1.1x10^7$ $e^-Å^{-2}$ (Fig. 2g). Thus, we were able to separate the intrinsic structural changes caused by electrochemical cycling to those due to the radiation damage. To do so, a combination of electron energy-loss spectroscopy (EELS) and atomic resolution HAADF-STEM studies are implemented at cryo-temperature to get new insights on the degradation of LNMO samples as a result of charging/discharging of the battery cells.

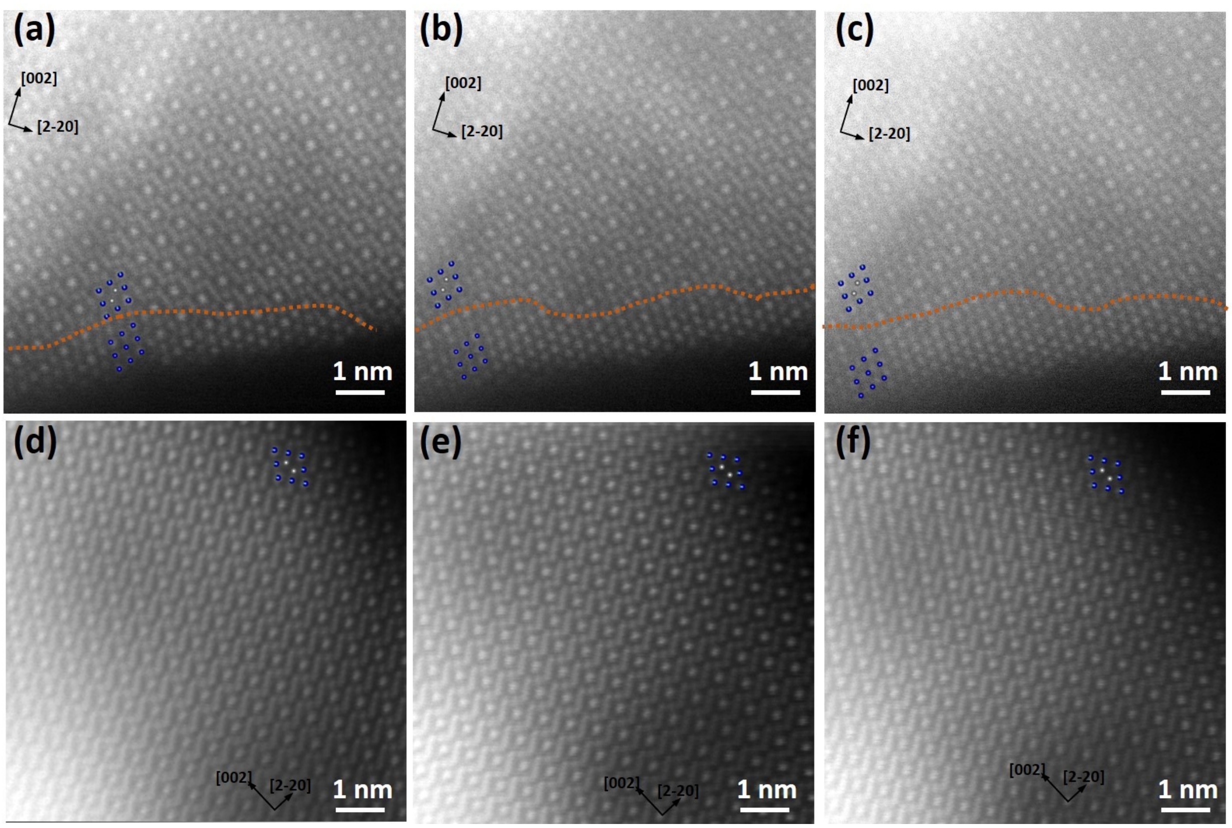

Figure 1. ***(a-c)*** *- HAADF-STEM images of $ZnCo_{1.8}Ni_{0.2}O_4$ nanoparticle imaged along [110] orientation acquired at room temperature with increasing cumulative electron dose: (a) – $5x10^5$ $e^-Å^{-2}$, (b) – $10^6 e^-Å^{-2}$, (c) – $1.5x10^6$ $e^-Å^{-2}$. Transformation from spinel to rocksalt phase on the surface area is observed. Orange line shows boundary between spinel and rocksalt phases with corresponding atomic structures overlaid.* ***(d-f)*** *- HAADF-STEM images of $ZnCo_{1.8}Ni_{0.2}O_4$ nanoparticle imaged along [110] orientation at cryogenic temperature acquired consecutively with doses: (d) 10^5 $e^-Å^{-2}$, (e) $6x10^5$ $e^-Å^{-2}$, (f) $2x10^6 e^-Å^{-2}$. The structure remains the same spinel.*

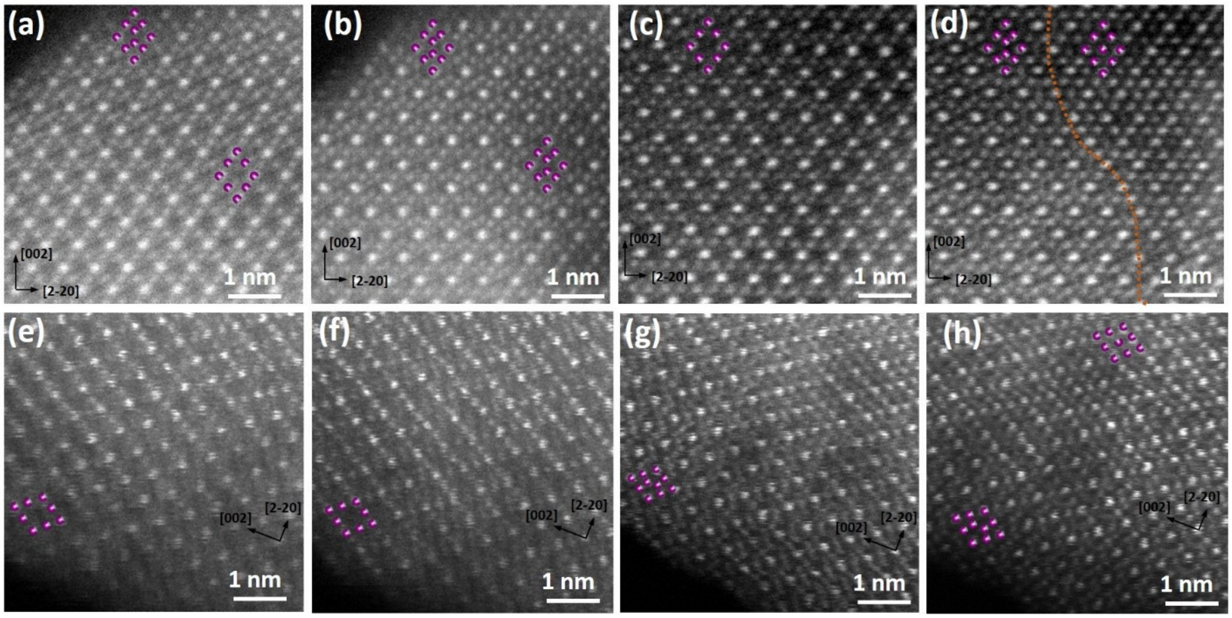

*Figure 2: **(a - d)** HAADF-STEM images of charged $LiNi_{0.5}Mn_{1.5}O_4$ nanoparticle imaged along [110] orientation obtained at room temperature. **(a)** – first image taken after alignment in the [110] zone axis, corresponding electron dose $5.5x10^5$ $e^-Å^{-2}$. Two phases are present in the viewing area: spinel and Mn_3O_4-like phase on the surface area. **(b)** – image acquired after $1.9x10^6$ $e^-Å^{-2}$ cumulative electron dose exposure, showing transformation into Mn_3O_4-like phase of the imaging area. **(c-d)** – images showing transformation from spinel into Mn_3O_4-like and rocksalt phases. (c) – mainly spinel phase is present, corresponding electron dose $9.6x10^5$ $e^-Å^{-2}$. (d) – image taken from the same area as (c) with $6.9x10^6 e^-Å^{-2}$ total dose: Mn_3O_4-like phase on the left side is separated from the rocksalt phase on the bulk by orange line. **(e-h)** HAADF-STEM images of charged $LiNi_{0.5}Mn_{1.5}O_4$ nanoparticle imaged along [110] orientation obtained at cryogenic temperature with electron doses: (e) - $5.4x10^5$ $e^-Å^{-2}$ showing the spinel phase only with corresponding structure overlaid, (f) – $2.5x10^6$ $e^-Å^{-2}$ –* structure remains spinel, *(g) – $1.1x10^7$ $e^-Å^{-2}$ – formation of Mn_3O_4-like phase on the surface can be observed, (h) - $1.3x10^7$ $e^-Å^{-2}$ - showing transformation of the surface area into the Mn_3O_4-like phase and rocksalt-like phase locally (the arrows show the unit cells with rocksalt phase).*

References

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[2] M. Lin et al, Chem. Mater., vol. 27, no. 1 (2015), p. 292.
[3] The authors acknowledge the Facilities for Analysis, Characterization, Testing and Simulations (FACTS) at Nanyang Technological University for access to TEM equipments as well as financial support from the Nanyang Technological University start-up grant (Grant M4081924). We also thank our colleagues from MSE-NTU, Rohit Satish, Rodney Chua Yong Sheng, and Madhavi Srinivasan for kindly providing the cycled LNMO particles, and Yan Duan and Zhichuan Jason Xu for kindly providing the ZCNO particles.