Atomic resolution enabled STEM imaging of nanocrystals at cryogenic temperature

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Abstract
In this study, we address the problem of electron-beam induced damage on two energy-related materials: LiNi$_{0.5}$Mn$_{1.5}$O$_4$ used as a cathode material for lithium-ion batteries and ZnCo$_{1.8}$Ni$_{0.2}$O$_4$ used as a catalyst for oxygen evolution reaction. Both materials were found to transform from the spinel into the rocksalt phase while being imaged by high-resolution scanning transmission electron microscopy (HR-STEM) at room temperature. To mitigate the degradation, we found HR-STEM characterization at cryogenic temperature delays the critical electron dose for structural modification. We determined the native phase of materials to be spinel while the other phases observed by HR-STEM were induced by the electron-beam. From a careful analysis of the experimental data and a detailed understanding of the different degradation processes induced by an energetic electron beam, we conclude that radiolysis is the mechanism responsible for the degradation in LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and ZnCo$_{1.8}$Ni$_{0.2}$O$_4$ nanoparticles.

1. Introduction
The interaction of an energetic electron beam with matter generates various signals that give information about the specimen under observation through both inelastic and elastic scattering mechanisms. The energy and/or momentum transferred to the specimen induces changes in the local structure, disturbing the local chemical bonding and eventually leading to a redistribution of the local atomic configuration [1]. Such modifications of the specimen under observation can lead to inaccurate conclusions; thus, electron-beam degradation mechanisms should be carefully addressed. They involve complex physical and chemical processes, namely radiation damage mechanisms: (i) knock-on damage, (ii) thermal damage caused by electron-beam heating, (iii) electrostatic charging, and (iv) radiolysis [2, 3].

Knock-on damage is caused by elastic scattering of electrons with the nucleus. As a result, if the momentum transferred from the incoming electron to the nucleus of the target atom is large enough, the atom is removed from its initial lattice position. This radiation damage is predominant in electrically conducting specimens, such as metals and some semiconductors [2]. The probability of radiation damage through the knock-on mechanism is reduced through the use of an accelerating voltage lower than a given threshold energy specific to the material under observation [4].

Thermal damage to a specimen is caused by the interaction of the incoming electron probe with the specimen via electron-phonon scattering, resulting in a local temperature increase [3]. However, the effect of the heating is negligible or, as for semiconductors, on the order of a few degrees. For example, in Si$_3$N$_4$ the temperature rise was found to be only 2.0 °C and 9.8 °C for 2.11 nA and 10.31 nA beam currents, respectively [5].

Electrostatic charging, a secondary effect of inelastic scattering, is due to the generation of secondary, backscattered and Auger electrons upon irradiation of a poorly conductive sample. The depletion of electrons at the probe position may result in a potential difference, relative to the surrounding areas, of up to 80 V [6]. A steady state potential of a few tens of volts is sufficient to modify the local charge per atom and consequently the overall energy balance of the crystal [6]. To prevent such an effect, conductive path should
exist from the area under observation to ground. It should be noted that for a semiconductor, the conductivity will decrease with decreasing temperature, resulting in an increase of the electrostatic charging at cryogenic temperature.

Radiolysis is the result of an inelastic interaction between the incident electron beam and the electron cloud of an atom. Radiolytic damage in oxides and transition metal oxides, the subject of this study, arises from the excitation of oxygen resulting in bond breakage, followed by the desorption of oxygen atoms at the surface, and finally reduction of the metallic cations [7–9]. As a result, radiolysis produces stable defects, atom displacement and breakage of chemical bounds [3]. Cooling of the specimen down to cryogenic temperature during transmission electron microscopy (TEM) observations reduces the atomic mobility and can consequently also reduce the radiolysis damage rate [1].

In practice, the simultaneous effects of the different beam-induced damage mechanisms make the mitigation of radiation damage challenging. The degradation mechanisms are also strongly material and voltage dependent. The knock-on damage can be reduced by using acceleration voltage below a threshold value for a given knock-on damage process. For example, the threshold energy for displacement of carbon atoms in graphene is 85 keV [4, 10], and therefore, an 80 keV probe mitigates such a degradation process when imaging graphene layers. On the other hand, transition-metal oxides show less degradation when imaged at high energies, as the knock-on threshold energy for these materials exceed the primary electron energy [1, 7]. For example, La0.7Sr0.3MnO3 shows less radiation damage when imaged at 200 keV compared to 80 keV [11] and Li2O3 was found to stand an electron dose 4–5 times larger when exposed to 200 keV electrons as opposed to 80 keV electrons [12]. However, at high electron energies, radiolysis damage becomes of prime importance [13].

There are various ways to delay radiation damage due to radiolysis, e.g. low-dose techniques, cooling the specimen to cryogenic temperature, encapsulation, or a combination of such techniques. It should be mentioned in most cases, the damage can be delayed but not eliminated [2]. For high resolution atomic (S)-TEM imaging, the sample must first be aligned in the desired zone-axis prior to observation, which by itself can consume a significant portion of the dose budget when nano/micro sized particles are involved. An innovative approach was used to observe beam-sensitive metal-organic framework (MOF) crystals by TEM. This approach is based on the acquisition of two diffraction patterns used to compute the necessary tilt to be applied to reach the zone axis of interest [14]. However, the implementation is not possible for an ensemble of nanocrystals due to the different orientations of the crystals resulting in a polycrystalline diffraction pattern. Low dose atomically resolved STEM imaging studies are rare, Mittelberger et al imaged carbon using 10^5 e− Å^-2 [15], still a large dose when electron-beam degradation is of concern. When low-dose techniques cannot be applied or are not sufficient to prevent electron-beam degradation, the investigation of the material at cryogenic temperature permits a larger electron dose before electron-beam degradation becomes visible [16–20]. High-resolution imaging at cryogenic temperature involves the use of low drift and low noise TEM holder capable of the needed resolution (~1 Å) combined with a double tilt capability. Recently, such a holder has become available, showing sub-angstrom information transfer and sufficient stability for atomic high-angle annular dark-field (HAADF) STEM imaging at cryogenic temperature [21].

In this study, we show the advantage of this double-tilt, cryogenic holder to investigate materials relevant for energy storage applications, namely LiNi0.5Mn1.5O4 (LNMO) used as a cathode in Li-ion batteries and ZnCo0.5Ni0.2O4 (ZCNO) used as catalyst for oxygen evolution reaction (OER) application.

2. Methods

High-resolution HAADF-STEM imaging was performed on an aberration-corrected JEOL ARM200F transmission electron microscope operating at 80 keV and 200 keV, with a convergence angle of 25 mrad and inner and outer collection angles of 68 and 280 mrad, respectively. For atomic-resolution imaging, the nanocrystals were tilted into zone axis in STEM mode. The HennyZ liquid-nitrogen double-tilt specimen holder was used for low temperature observations [21]. The temperature at the tip of the holder was around 140 K. Samples were drop-casted onto conventional lacey carbon TEM grids or MEMS-chips for low temperature observations. HAADF-STEM image simulations were done with Dr. Probe software [22], with parameters used for imaging during experiments.

Details on the synthesis of ZCNO particles are given elsewhere [23], and the particles were studied as produced. Spinel LNMO (99.9%) material was purchased from Sigma Aldrich and was mixed with conducting carbon (Super P, TIMCAL) in a 9:1 ratio by weight. The mixture was then dried in a Buchi oven for 12 h at 80 °C in vacuum. The electrolyte used in the cell was 1 M solution of LiPF6 dissolved in a 1:1 ratio by volume of ethylene carbonate: diethylene carbonate. The prepared cells were tested on an Arbin BT 2000 at a current rate of 20 mAg⁻¹ and cycled between 3.5 and 5 V versus Li.

In the rest of the manuscript acronym STEM refers to HAADF-STEM, unless otherwise stated.
Figure 1. Atomic structural models in the [110] projection of the (a) spinel \( \text{ZnCo}_{1.8}\text{Ni}_{0.2}\text{O}_4 \) and (b) rocksalt CoO phases. The dotted circles show the positions of the tetrahedral and octahedral sites for the spinel and rocksalt phases respectively. STEM images simulations of the (c) spinel (Fd-3m) and (d) rocksalt (Fm-3m) phases of \( \text{ZnCo}_{1.8}\text{Ni}_{0.2}\text{O}_4 \) and CoO overlapped with the corresponding atomic models.

3. Results

3.1. \( \text{ZnCo}_{1.8}\text{Ni}_{0.2}\text{O}_4 \)

\( \text{ZnCo}_{1.8}\text{Ni}_{0.2}\text{O}_4 \) is a promising novel spinel-oxide catalyst for OER applications \[23\]. Currently there are few TEM studies of spinel oxide family materials applied to OER for hydrogen fuel production by electrochemical water splitting \[24\]. \( \text{ZnCo}_{1.8}\text{Ni}_{0.2}\text{O}_4 \) is representative of the \( \text{ZnCo}_2\text{O}_4 \) (ZCO) spinel oxide material (Fd-3m), obtained by doping Ni into Co sites. In ZCO, \( \text{Zn}^{2+} \) atoms occupy tetrahedral sites and \( \text{Co}^{3+} \) atoms stay in the octahedral sites \[25\], whereas in ZCNO, Ni metal cations partially substitute \( \text{Co}^{3+} \) cations. The [110] projection of the crystal structure, chosen for STEM studies, allows separate imaging of the Co(Ni) and Zn atomic columns. Along this projection, eight Co(Ni) atomic columns form a diamond-like pattern with two distinct atomic columns that differ by their atomic density, columns denoted as Co(Ni)-1 have twice as many atoms as Co(Ni)-2 columns (figure 1(a)). Therefore, Co(Ni)-1 appear brighter on STEM images than Co(Ni)-2 ones (figure 1(c)). Two tetrahedral sites in the middle of the diamond-like pattern are occupied by Zn atoms. Intensity of Zn atomic columns and Co(Ni)-2 ones is alike due to similar average atomic number along the [110] projection.

In the rocksalt structure the cations form a face-centered cubic arrangement with the anions occupying all the octahedral sites. An example of a typical rocksalt structure similar to ZCNO is CoO (figure 1(b)). In the rocksalt structure, the middle octahedral site is occupied by transition metal atoms (Co in the case of CoO structure). In addition, for this structure all atomic columns have the same number of atoms, and thus the same density. The simulated STEM image of the CoO rocksalt phase is given in figure 1(d) instead of the one for ZCNO for which the distribution of the cations in rocksalt phase is unknown.

3.1.1. Room temperature observations of \( \text{ZnCo}_{1.8}\text{Ni}_{0.2}\text{O}_4 \)

Figure 2 shows STEM images of ZCNO nanoparticle along the [110] direction recorded at room temperature. Figure 2(a) was taken just after the alignment into the zone axis. The electron dose used to obtain the image is \( 5 \times 10^5 \text{ e}^- \text{Å}^{-2} \) (excluding the electron dose for zone axis alignment). The atomic structure matches with the spinel phase, except for ~1 nm of rocksalt structure on the bottom right near the surface (denoted by white boxed area in figure 2(a)). A line profile of the STEM intensity across the diagonal of the diamond-like structure is shown on figure 2(c). The line profile was extracted from the yellow rectangle indicated in figure 2(b). The two most intense peaks correspond to the Co(Ni)-1 atomic columns, while the two peaks with a lower intensity correspond to Zn columns. The difference in intensity between the two types of Co(Ni) columns matches the simulations shown in figure 1(c), and is due to the difference in density between them.

Figure 2(d) was taken consecutively after figure 2(a), with an accumulated electron dose of \( 10^6 \text{ e}^- \text{Å}^{-2} \). The transformation from the spinel to the rocksalt phase is seen on ~2 nm surface region and separated by a blue dashed line (figure 2(d)). An increase of the contrast at middle of the unit cell, where two Zn atomic columns (tetrahedral sites) were observed in figure 2(a) is also visible in the spinel side (next to the blue...
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Figure 2. STEM images of ZnCo$_{1.8}$Ni$_{0.2}$O$_4$ nanoparticle imaged along [110] orientation at room temperature. (a) First image taken after alignment in the [110] zone axis with a total electron dose of $5 \times 10^5$ e$^-\text{Å}^{-2}$. The white rectangle on the bottom right shows the presence of the rocksalt-like structure. (b) Magnified image of (a) overlaid with the spinel atomic model. The yellow rectangle indicates where the line profile shown in (c) was extracted from. (c) Line profile of the STEM intensity shown in (b). The rectangular box indicates the atomic columns shown in the line profile, the two most intense peaks are due to the Co(Ni) columns, the two middle peaks are from the Zn columns. (d) Image taken consecutively to image (a), corresponding cumulated electron dose $10^6$ e$^-\text{Å}^{-2}$. Transformation from spinel to rocksalt phase on the surface area is clearly observed (blue line shows boundary between spinel and rocksalt phases). (e) Magnified image of (d) overlaid with the rocksalt atomic model. (f) Line profile of the STEM intensity, shown in (e). The rectangular box indicates the atomic columns shown in the line profile.

Figure 3. STEM images of ZnCo$_{1.8}$Ni$_{0.2}$O$_4$ nanoparticle imaged along [110] orientation at cryogenic temperature. (a) First image taken after alignment in the [110] zone axis with a total electron dose of $4.3 \times 10^5$ e$^-\text{Å}^{-2}$. (b) Magnified image of (a) overlaid with the spinel atomic model. The yellow rectangle indicates where the line profile shown in (c) was extracted from. (c) Line profile of the STEM intensity shown in (b). The rectangular box indicates the atomic columns shown in the line profile, the two most intense peaks are due to the Co(Ni) columns, the two middle peaks are from the Zn columns. (d) Image taken consecutively to image (a), corresponding cumulated electron dose $2 \times 10^6$ e$^-\text{Å}^{-2}$. Transformation from spinel to rocksalt phase on the surface area is clearly observed (blue line shows boundary between spinel and rocksalt phases). (e) Magnified image of (d) overlaid with the spinel atomic model. (f) Line profile of the STEM intensity, shown in (e). The rectangular box indicates the atomic columns shown in the line profile, the two most intense peaks are due to the Co(Ni) columns, the two middle peaks are from the Zn columns.

dashed line). A contrast from a single atomic column is now visible in the octahedral site, which indicates the ~2 nm surface region transformed into the rocksalt phase.

It should be noted that the intensity of all the columns is equivalent, indicating a homogeneous distribution of the Co, Ni and Zn species, in the rocksalt structure. By comparing figures 2(a) and (d), it is clear that the rocksalt phase is due to the degradation of the spinel phase by the electron beam. However, it is not possible to conclude whether rocksalt phase observed in figure 2(a) is the result of electron-beam degradation or if the rocksalt phase was originally present on the nanoparticle. Such uncertainty about the presence of rocksalt phase in the raw material makes it difficult to draw any conclusion between the OER properties and the microstructure. Thus, STEM-based analyses that aim to link the structure and the catalyst performance cannot succeed if electron-beam degradation is not mitigated.

3.1.2. Cryogenic temperature observations of ZnCo$_{1.8}$Ni$_{0.2}$O$_4$

In order to delay the degradation of the ZCNO nanoparticles under electron beam irradiation, STEM imaging at cryogenic temperature is implemented. Figure 3 shows STEM images recorded at cryogenic temperature of ZCNO nanoparticle along the [110] direction. Figure 3(a) was taken just after the alignment into the zone axis, with an electron dose of $4.3 \times 10^5$ e$^-\text{Å}^{-2}$ used to obtain the image (excluding the electron dose for zone axis alignment). Only the spinel phase is visible. Figure 3(d) was taken after a cumulative dose of $2 \times 10^6$ e$^-\text{Å}^{-2}$ from the same area as of figure 3(a). The structure maintains the same spinel phase. The extracted line profiles of both images show tetrahedral sites have the same relative contrast representative of the spinel phase.
Figure 4. (a) Lithiated and (b) delithiated LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinel atomic models in the [110] projection. STEM simulated images of the (c) spinel (Fd-3m), (d) rocksalt and (e) Mn$_3$O$_4$-like phases of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ overlapped with the corresponding atomic models.

3.2. LiNi$_{0.5}$Mn$_{1.5}$O$_4$

LNMO is considered to be a promising cathode material for Li-ion batteries. However, various factors such as oxidation state, atomic coordination of Mn and Ni cations and the morphology of the particles influence its performance as a cathode material [26, 27].

LNMO has a cubic spinel structure (Fd-3m) with lattice constants $a = 8.17$ Å [28]. Upon charge/discharge cycling, it goes from the lithiated (pristine) to delithiated (charged) state, respectively. Figure 4 shows the atomic structures viewed along the [110] direction for both lithiated and delithiated states. The [110] projection is chosen for the STEM studies because the Mn(Ni) atomic columns can be imaged separately from the Li. Mn and Ni atoms occupy the same lattice positions (16c octahedral sites, Mn(Ni)-1, Mn(Ni)-2) and are represented in purple and grey colour, respectively in the structural model (figure 4). Atomic columns of Mn(Ni)-1 are twice as dense as those of Mn(Ni)-2. Li columns occupy the tetrahedral 8d sites. The structural model of the spinel structure of LNMO is overlaid to the STEM image simulation (figure 4(c)). Two distinct contrasts from the Mn/Ni atomic columns, forming diamond-like pattern, are seen due to the different density of the Mn(Ni)-1 and Mn(Ni)-2 columns. It should be noted that, there is no contrast at Li-tetrahedral sites nor at the middle octahedral site for the spinel phase.

Previous STEM studies of LNMO have established a relation between the appearance of different crystallographic phases and the state of charge [29]. In addition to the spinel phase (with the Li atoms at the tetrahedral sites), the Mn$_3$O$_4$-like (spinel but with the tetrahedral sites occupied by Mn atoms, figure 4(e)) and rocksalt (figure 4(d)) phases have been reported. It was claimed that upon delithiation (first charge), transition metal atoms (Mn/Ni) move into the Li-tetrahedral sites, forming Mn$_3$O$_4$-like structure on the surface region and the rocksalt phase on the subsurface [29]. However, the STEM images of the reported results does not support the degradation mechanism claimed by the authors. On the other hand, electron-beam induced transformation from spinel to rocksalt phase and from layered (R-3m) to rocksalt (Fm-3m) were reported for LiMn$_2$O$_4$ [30] and LiNi$_{0.4}$Mn$_{0.5}$Co$_{0.18}$Ti$_{0.02}$O$_2$ (NMC) [31] cathode materials respectively. LNMO has the same spinel structure as LiMn$_2$O$_4$, except for the presence of Ni atoms, so a similar electron beam-induced degradation is likely to happen while imaging with TEM techniques.

3.2.1. Room temperature observations of LiNi$_{0.5}$Mn$_{1.5}$O$_4$

Figure 5 shows STEM images of a delithiated LNMO nanoparticle along the [110] zone axis. Figure 5(a) was taken just after the alignment into the zone axis, two different phases are present with their boundary depicted by a dashed blue line. The subsurface region of the particle (on the right side of the dashed blue
Figure 5. STEM images of charged LiNi$_{10}$Mn$_{10}$O$_{22}$ nanoparticles imaged along [110] orientation recorded with an electron-beam energy of 200 keV at room temperature. (a) First image taken after alignment in the [110] zone axis with a total electron dose of $8.7 \times 10^{5}$ e$^{-}$/Å$^{2}$. Two phases are present in the viewing area: spinel phase and Mn$_{10}$O$_{22}$-like phase on ~2–3 nm surface separated by blue dashed line. (b) Magnified image of (a) overlaid with the spinel atomic model. The yellow rectangle indicates where the line profile shown in (c) was extracted from. (c) Line profile of the STEM intensity shown in (b). The rectangular box indicates the atomic columns shown in the line profile, the two most intense peaks are due to the Mn/Ni columns. (d) Image taken consecutively to image (a), corresponding cumulated electron dose $1.3 \times 10^{6}$ e$^{-}$/Å$^{2}$. Transformation from spinel to rocksalt phase is clearly visible. (e) Magnified image of (d) overlaid with the rocksalt atomic model. (f) Line profile of the STEM intensity, shown in (e). The rectangular box indicates the atomic columns shown in the line profile.

line) shows mainly the spinel structure (with no visible contrast in the middle of the diamond-like pattern). The associated line profile (figure 5(c)), taken from the spinel phase shows only two main peaks from the Mn(Ni)-1 columns, with no signals from the tetrahedral sites. The surface regions (~2–3 nm from the surface) show additional contrast in the middle at the Li-tetrahedral sites that are supposed to be empty for the delithiated LNMO. The lithiation/delithiation process may not be homogeneous or complete through the entire cathode material, so the presence of Li atoms in the tetrahedral sites cannot be excluded. For the lithiated LNMO, the STEM simulated image shows the absence of contrast at the Li-tetrahedral sites (figure 4(c)). Thus, any contrast inside the diamond-like pattern, including the Li-tetrahedral and octahedral sites, is due to the presence of transition metal atoms and associated with the Mn$_{10}$O$_{22}$-like or rocksalt phases. In the bulk of the particle no contrast is observed inside the diamond-like pattern, indicating the presence of the spinel phase.

Figure 5(d) was taken consecutively after figure 5(a) at the same area, with a total cumulative dose of $1.3 \times 10^{7}$ e$^{-}$/Å$^{2}$. The transformation of the structure is clearly visible in the subsurface region. The region showing two atomic columns inside the diamond-like pattern (due to migration of transition metal atoms (Mn/Ni) into Li-tetrahedral sites) corresponds to the Mn$_{10}$O$_{22}$-like phase while the presence of a single contrast is the signature of the rocksalt phase. Such a contrast is seen from the line profile along the (002) direction (figure 5(f)) and can be attributed to the rocksalt structure. In addition, part of the particle which had a Mn$_{10}$O$_{22}$-like phase (figure 5(a)) on its surface region stayed unchanged on the second image (figure 5(d)). It is clear these particles are not stable under electron-beam irradiation under such conditions. This makes the determination of the initial state of the crystal difficult.

In an attempt to decrease the effect of radiation damage, the LNMO particles were imaged with an 80 keV electron beam. The results of this experiment are represented as a set of images acquired with increasing electron dose (figure 6). Figure 6(a) shows the first image acquired at 80 keV, two phases are present: the spinel and Mn$_{10}$O$_{22}$-like phases at the surface. With increasing electron dose (figure 6(d)), the amount of the Mn$_{10}$O$_{22}$-like phase increases. For a cumulative electron-dose of $1.95 \times 10^{7}$ e$^{-}$/Å$^{2}$ the rocksalt phase starts to be visible (purple boxed area shown in image 6(g)). Even under electron beam irradiation at 80 keV the phase transformations from spinel to Mn$_{10}$O$_{22}$-like and, finally, to rocksalt phase is observed. It can be also noticed that the phase transformation is accompanied by a significant change of contrast likely to be associated with a mass-loss due to the removal of O and transition metal atoms under irradiation. This change of contrast was not observed when imaged with a 200 keV beam and could be related to different degradation mechanism taking place at 80 keV and 200 keV.

3.2.2. Cryogenic temperature observations of LiNi$_{0.5}$Mn$_{1.5}$O$_{4}$

Figure 7 shows consecutively acquired STEM images of LNMO particles at cryogenic temperature. Figure 7(a) is the first image taken after the alignment to the [110] zone axis. In this image, and unlike for the images acquired at room temperature, only the spinel phase is observed. Figure 7(c) is the STEM image acquired from the same area after an exposure to $2.5 \times 10^{6}$ e$^{-}$/Å$^{2}$. The appearance of additional contrast at Li-tetrahedral sites is observed and better seen on the line profile along (002) direction (figure 7(d)). When the total irradiation dose reached $1.3 \times 10^{7}$ e$^{-}$/Å$^{2}$ (figure 7(e)), the surface of nanoparticle is transformed into the Mn$_{10}$O$_{22}$-like phase, and the subsurface area locally transform into the rocksalt phase. The presence of
Figure 6. STEM images of charged LiNi$_{0.5}$Mn$_{1.5}$O$_4$ nanoparticle imaged along [110] orientation at room temperature recorded with an electron-beam energy of 80 keV. (a) First image acquired after alignment in the zone axis, corresponding electron dose exposure $3.25 \times 10^5 \text{ e}^{-}\text{Å}^{-2}$. Two phases are present: spinel and Mn$_3$O$_4$-like phase at ~1–2 nm surface area. (b) Magnified image of (a) with Mn$_3$O$_4$-like atomic model shown on the surface. The yellow rectangle indicates where the line profile provided in (c) was taken from. (c) Line profile of the STEM intensity shown in (b). (d) Image from the same area as in (a), taken after $1.35 \times 10^7 \text{ e}^{-}\text{Å}^{-2}$ electron dose. The amount of Mn$_3$O$_4$-like phase (shown by the boxed area) increased and the spinel transforms into Mn$_3$O$_4$-like phase. The change in contrast is attributed to a mass loss under irradiation. (e) Magnified image of (d) overlaid with the Mn$_3$O$_4$-like atomic model. (f) Line profile of the STEM intensity, shown in (e). (g) Image taken after $1.95 \times 10^7 \text{ e}^{-}\text{Å}^{-2}$. The area denoted by the boxed area near the surface fully transformed into the rocksalt phase. (h) Magnified image of (g) overlaid with the rocksalt atomic model. (i) Line profile of the STEM intensity from the rectangular box in (h). The appearance of additional contrast at the middle is attributed to the formation of rocksalt phase.

Figure 7. STEM images of charged LiNi$_{0.5}$Mn$_{1.5}$O$_4$ nanoparticle imaged along [110] orientation recorded with an electron-beam energy of 200 keV at cryogenic temperature. (a) First image taken after alignment in the [110] zone axis with a total electron dose of $5.4 \times 10^5 \text{ e}^{-}\text{Å}^{-2}$ showing only the spinel phase. (b) Line profile of the STEM intensity from the rectangular box in (a). (c) Image taken consecutively to image (a), corresponding to a accumulated electron dose of $2.5 \times 10^6 \text{ e}^{-}\text{Å}^{-2}$. (d) Line profile of the STEM intensity from the rectangular box in (c). The appearance of an additional contrast at the Li-tetrahedral sites is attributed to the formation of the Mn$_3$O$_4$-like phase. (e) Image taken consecutively to image (c), corresponding to a cumulated electron dose of $1.3 \times 10^7 \text{ e}^{-}\text{Å}^{-2}$ showing transformation of the surface area into the Mn$_3$O$_4$-like phase (strong contrast observed at Li-sites) and rocksalt-like phase locally. The arrows show the presence of additional contrast at the centre of the diamond-like pattern. (f) Line profile of the STEM intensity from the rectangular box in (e). The appearance of an additional contrast at the middle is attributed to the formation of the rocksalt phase.

the rocksalt phase is shown by arrows in figure 7(e) and is highlighted by the presence of an extra peak in the middle of the line profile (figure 7(f)).

4. Discussion

The previous two examples have shown successful imaging of beam sensitive materials relevant for energy applications at cryogenic temperature to mitigate the electron-beam degradation. The systematic comparison of the effect of the electron beam at room temperature and at cryogenic temperature allows discussion of the possible mechanism responsible for the degradation of LNMO and ZCNO materials. Transition metal oxides are poor electron conductors, and thus their electrical conductivity decreases with decreasing temperatures. The mitigation of the effect of the electron beam at cryogenic temperature indicates electrostatic charging is not the main degradation mechanism when imaging LNMO and ZCNO. We have also shown that a lower acceleration voltage increases the effect of degradation when imaging LNMO particles (ZCNO particles were too thick to be imaged at atomic resolution with 80 keV electrons), which indicates the knock-on threshold energy for LNMO is not in the 80–200 keV energy range, and thus not responsible for the degradation in this study. From the four degradations mechanism discussed in the introductory section, radiolysis and thermal damage are the two mechanisms most mitigated by low temperature imaging. The thermal heating by the
electron beam is on the order of tens of degrees; thus, it is suppressed by imaging at cryogenic temperature. We have observed that imaging at cryogenic temperature delays the irradiation damage but does not eliminate it, so damage through the thermal effect is not likely to be the main source of degradation.

Radiolysis has been suggested to be responsible for bond breakage in oxides and transition metal oxides followed by the desorption of oxygen atoms at the surface and finally reduction of the metallic cations. The reduction of the atomic mobility at lower temperature makes the desorption of oxygen atoms less energetically favourable, thus requiring a larger electron dose to induce the same degradation compare to irradiation at room temperature. In the view of the arguments discussed in this section, radiolysis is the most probable effect responsible for the electron-beam degradation of LNMO and ZCNO nanoparticles.

5. Conclusions

In this work, we investigated the effect of the electron beam on the structural transformations of materials relevant for energy applications: LNMO used as cathode in Li-ion batteries and ZCNO as catalyst for OER applications. Results show that both materials are prone to structural changes during STEM imaging due to irradiation damage when imaged at room temperature using 200 keV electrons, as well as 80 keV for LNMO sample. Both materials have spinel structure that transform into rocksalt phase upon irradiation. Implementation of cryogenic-STEM investigations show an increase of critical dose (by 3 times in the case of LNMO and at least 4 times in case of ZCNO) needed to cause transformations. This work highlights the importance of careful design of STEM experiments, especially when studying materials prone to structural changes.

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References

[1] Hobbs L W 1979 Radiation effects in analysis of inorganic specimens by TEM Introduction to Analytical Electron Microscopy, ed J J Hren, J I Goldstein and D C Joy (New York: Springer) pp 437–80
[2] Egerton R F 2019 *Micron* 119 72–87
[3] Egerton R F, Li P and Malac M 2004 *Micron* 35 399–409
[4] Egerton R F 2014 *Ultramicroscopy* 145 85–93
[5] Liu B, Dong Z L, Hua Y, Fu C, Li X, Tan P K and Zhao Y 2018 *AIP Adv.* 8 115327
[6] Caraux J 1995 *Ultramicroscopy* 60 411–25
[7] Jiang N 2016 *Rep. Prog. Phys.* 79 016501
[8] Shim J-H, Kang H, Kim Y-M and Lee S 2019 *ACS Appl. Mater. Interfaces* 11 44293–9
[9] Johnston-Peck A C, DuChene J S, Roberts A D, Wei W D 2016 *Ultramicroscopy* 170 1–9
[10] Meyer J C et al 2012 *Phys. Rev. Lett.* 108 196102
[11] Nord M, Vullum P E, Hallsteinsen I, Tybell T and Holnestad R 2016 *Ultramicroscopy* 169 98–106
[12] Basak S, Jansen J, Kabiri Y and Zandbergen H W 2018 *Ultramicroscopy* 188 52–58
[13] Egerton R F 2013 *Ultramicroscopy* 127 100–8
[14] Zhang D, Zhu Y, Liu L, Ying X, Hsiung C-E, Sougrat R, Li K, Han Y 2018 *Science* 359 675–9
[15] Mittelberger A, Kramberger C, Hofer C, Mangler C and Meyer J C 2017 *Microsc. Microanal.* 23 809–17
[16] Kim Y-J, Tao R, Klie R F and Seidman D N 2019 *ACS Nano* 7 732–9
[17] Zachman M J, Tu Z, Choudhury S, Archer L A and Kourkoutis I F 2018 *Nature* 560 345–9
[18] Yu S-H, Zachman M J, Kang K, Gao H, Huang X, DiSalvo F J, Park J, Kourkoutis I F, Abruna H D 2019 *Adv. Energy Mater.* 9 1902773
[19] Spoth K A, Zachman M J, Muller D A and Kourkoutis I F 2019 *Microsc. Microanal.* 25 1660–1
[20] Li Y et al 2017 *Science* 358 506–10
[21] Bell D and Zandbergen H 2016 *European Microscopy Congress Conf. Proc.* pp 352–3
[22] Barthel J 2018 *Ultramicroscopy* 193 1–11
[23] Duan Y et al 2019 *Adv. Mater.* 31 1807898
[24] Kim J S, Kim B, Kim H and Kang K 2018 *Adv. Energy Mater.* 8 1702774
[25] Parida P, Kashikar R, Jena A and Nanda B R K 2018 *J. Phys. Chem. Solids* **123** 133–49
[26] Duncan H, Hai B, Leskes M, Grey C P and Chen G 2014 *Chem. Mater.* **26** 5374–82
[27] Qiao R, Wray L A, Kim J-H, Pieczonka N P W, Harris S J and Yang W 2015 *J. Phys. Chem. C* **119** 27228–33
[28] Pasero D, Reeves N, Pralong V and West A R 2008 *J. Electrochem. Soc.* **155** A282
[29] Lin M et al 2015 *Chem. Mater.* **27** 292–303
[30] Gao P, Ishikawa R, Tochigi E, Kumamoto A, Shibata N and Ikuhara Y 2017 *Chem. Mater.* **29** 1006–13
[31] Lin F, Markus I M, Doeff M M and Xin H L 2014 *Sci. Rep.* **4** 5694