

Manganese Migration in Pristine $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ Observed by Differential Phase Contrast

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Abstract

LiMn_2O_4 has been considered one of the most promising cathode materials for Li-ion batteries due to its thermal stability, abundance, environmental affinity and the possibility to exchange Li-ions in a three-dimensional fashion. However, it still suffers from major problems such as capacity fading and voltage decay, which has been associated to phase transformations and dissolution of transition metals. In this report, we use scanning transmission electron microscopy and differential phase contrast (DPC) to obtain new insights in the structural characteristics of $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ to better understand the mechanisms behind the structural transformation in LiMn_2O_4 . We exploit the fact that DPC has the ability to observe simultaneously light and heavy elements, measure projected electric fields and charge distribution at the atomic level. This approach allow us to monitor the migration of very low amounts of Mn to the Li atomic columns at the surface and subsurface regions, which otherwise will be very challenging to observe using other techniques such as HAADF and ABF. These observations not only provide fundamental understanding of the structure of LiMn_2O_4 , but also reveal DPC as a novel technique to determine local structural changes in materials consisting of heavy and light elements, localise light elements, monitor low concentrations of substitutional species and identify phase transformations.

Introduction

Recently, differential phase contrast in scanning transmission electron microscopy (STEM-DPC) has taken an important role on the characterization of materials at the atomic level due to its ability to simultaneously detect light and heavy elements and retrieve information about the interaction of the electron beam with the atomic electric field of the samples. This, in turns, provides the ability to observe the structure of materials and obtain critical information about the projected potential,¹ electric field,^{2 3 4} and charge distribution.^{2 5} With such capabilities, it may be possible to study local structural changes in materials consisting of heavy and light elements, localise light elements, monitor low concentrations of substitutional species and identify phase transformations.

In the case of spinel cathodes for Li-ion batteries, structural modifications such as the diffusion of the transition metal to Li positions have been shown to have a detrimental effect on the functional properties of these materials due to capacity loss⁶. These materials have been extensively studied at the atomic scale, using high-angle annular dark-field (HAADF) STEM due to the interpretation of mass-thickness contrast images. However, this technique is not able to provide information about the position of light elements such as Li, especially when low amounts of Li are substituted by transition metal.

$\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ is a well-known candidate cathode material for lithium-ion batteries because of its ability to exchange Li-ions in a three-dimensional spinel structure. However, one of the major challenges with this material is the capacity loss, attributed to the dissolution of Mn to the electrolyte⁷. In fact, several studies have reported the transformation of $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ spinel structure to rocksalt structure. Amos et. al⁸, for instance, have demonstrated a surface reconstruction in this material, where a stable surface is formed followed by a $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ subsurface with retention of bulk $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$. Other studies have shown Mn mobility to tetrahedral positions, promoting capacity loss due to changes in the structure.⁹

For this reason, we propose in this work to use STEM-DPC to monitor the manganese migration in $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$. To accomplish this, we use the electron beam to assist the migration of Mn atoms and assess whether STEM-DPC is sensitive to probe small variations in the structure, in particular, in-column atomic substitutions. We use pristine $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ to image both heavy and light atoms simultaneously, thus providing information on the local modification of the structure and distribution of Li, Mn and O species. We demonstrate the ability of STEM-DPC to detect very low substitutions of Li by Mn at the materials surface and subsurface regions, which otherwise will be

very challenging to observe using other techniques such as HAADF and ABF. Therefore, STEM-DPC was used to monitor the migration of Mn and observe local regions depleted in Li and the existence of manganese atoms in 1) tetrahedral sites occupying a typical Li atom position and/or 2) a free octahedral site. Simulated DPC-STEM images obtained by multisliced calculations in conjunction with DFT calculations of the projected potential and electric field were performed to confirm the experimental images. These findings contribute to a fundamental understanding of the mechanisms of lithium and manganese exchange in $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ spinel structures.

RESULTS AND DISCUSSION

Differential phase contrast in pristine $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$

Pristine $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ nanoparticles exhibit a well-known cubic spinel structure, where Li atoms occupy tetrahedral sites (8a) and Mn has preferential occupancy for octahedral sites (16d). When viewed along the [0 1 1] direction, the atomic species (Mn, Li and O) can be easily observed as independent atomic columns using STEM mode. **Figure 1** shows an example of a HAADF image of a pristine $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ structure, showing good agreement with multisliced computer simulations (inset). The images clearly display the presence of Mn atomic columns forming a diamond-like symmetry (highlighted by the yellow line), where the Mn columns located at the corners of the yellow diamonds have brighter contrast due to a higher Mn occupancy in these positions. On the other hand, Li and O are not observed due to the low atomic number of these species. However, it has been recently reported that lighter elements such as H, Li and O can be imaged simultaneously with heavy elements using annular bright-field STEM-ABF^{10 11} and STEM-DPC^{12 13} techniques. The latter has stood out over other STEM techniques due to the low dose requirements¹ and the ability of revealing the (projected) potential (iDPC), electric field (eDPC) and charge distribution (dDPC), despite the fact that very thin samples are required. To demonstrate these capabilities, simulated images of $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ were calculated using the multisliced method for one unit cell (**Figure 2**), as well as other thicknesses, as shown in the supplementary information (**Figure S1**). In contrast to the HAADF simulations, the DPC-based calculations are capable of detecting Li and O atomic columns. A careful analysis of the dDPC calculations show the identification of Li atomic column for very thin samples as highlighted in **Figure 2** and thick samples **Figure S1**, revealing its flexibility. Among the various signals (iDPC, eDPC and dDPC), dDPC seems to be the most appropriate for identifying the signal of both heavy and light elements simultaneously. Yet, the contrast changes as a function of sample thickness due to multiple scattering and coherent interference at low collection angles.

In general, it should be noted that to better interpret the contrast, the proportionality of DPC with respect to the projected electric field, and therefore to the potential and charge distribution, is limited to a (weak) phase object approximation¹⁴, and thus very thin samples. This proportionality can be observed by the linear behaviour of the intensity of the eDPC signal as a function of thickness, (Figure 3), which is observed to occur up to a thickness of approximately 3 nm for a LiMn_2O_4 crystal oriented along the [0 1 1] direction. For a thickness greater than 3 nm the eDPC average signal is no longer linearly proportional to the thickness, due to dynamical scattering effects¹⁵. Indeed, such effects also depend on the structure of the material and the mass of the chemical species present. As a result, the interpretation of the contrast at thicknesses beyond the linear regime becomes more difficult to assess.

To better visualize the linear dependence of the eDPC signal and thickness, we consider a hypothetical model consisting of atoms with atomic numbers Z ranging from 1 to 98, distributed as in the periodic table (Figure 4). Subsequently, we have calculated the evolution of the eDPC intensity as a function of the number of atoms in a single column. This is shown for the elements Li, Mn and O in Figure 4b. It is clear that for each element the evolution of the eDPC intensity as a function of the number of atoms in a single column differs. Yet, despite the deviation from linearity beyond a specific thickness, useful information regarding the location of the various elements can still be retrieved. For instance, as shown in Figure 4b, for the case of Li and Mn columns with 11 atoms each, Li will appear more intense than Mn, facilitating the identification of Li. This can be also observed in the LiMn_2O_4 system using multisliced simulations, as well as experimental results, where the signal for Mn in sites with higher occupancy becomes weaker for thicker samples, allowing better observation of oxygen and lithium (Figure S2).

Having in mind the aforementioned multisliced computer simulations for pristine $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$, DPC experimental images were obtained from an actual sample, as shown in Figure 5. Annular dark-field (ADF) images, and DPC images obtained from the segmented detector are shown in Figures 5a to 5c. These DPC raw images can be interpreted as the deflection of electrons along the x and y directions (see the illustration of the segmented detector in the inset of Figures 5b and c), as a function of the local intrinsic electric field. The white contrast indicates deflection along the positive direction, whereas the black contrast reflects a deflection in the negative direction, assuming the reference coordinate system defined in the inset of Figures 5b and c. Such deflection is proportional to the electric field of the sample if the electron velocity in the z direction doesn't change significantly, which is the case for very thin non-magnetic samples, due to the Lorentz force experienced by the electrons when passing through the sample³. Having the information of the electric field, the potential (by means of integration) and the charge distribution (by means of differentiation) can be

obtained^{1 2 3 4 5}. Thus, the images proportional to the projected potential - iDPC, the projected electric field - eDPC, and the projected charge distribution - dDPC, were calculated using the experimental repeated-unit average image, as shown in Figure 6. Figure 6a and 6f show the experimental and simulated ADF images of a small section of the sample oriented along the [0 1 1] direction, where the diamond-like symmetry is clearly observed. Additional contrast can be detected for the O columns due to the lower collection angles, compared to a typical HAADF image. Figures 6b and 6g show the experimental and simulated images for the projected atomic electric field (eDPC), in which the brighter regions represent a higher magnitude of the field, with the corresponding direction represented by the colour wheel (Figures 6c and 6h). Whereas Figures 6d and 6e show the projected charge distribution and projected electrostatic potential. The results shown in Figure 6 reveal a good agreement between the simulated and the experimental images. The atomic electric field (eDPC) due to the Mn and O are clearly identified, whereas dDPC images offer better contrast to identify the Li atomic columns. For comparison, a computer simulation where a complete Li atomic column was removed from the LiMn_2O_4 spinel structure is shown in supplementary information (Figure S3) to validate capability of technique to observe lithium. In addition, DFT calculations were carried out for one unit cell of $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ oriented along the [0 1 1] direction, and the projected electric field, charge distribution and electrostatic potential were calculated, as shown in Figures 6k to 6n. The DFT calculations show also a very good agreement with the DPC results.

Manganese Migration in Pristine $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$

Structural changes in $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ can be induced by transferring sufficient energy to the system, which may cause unwanted phase transformations that affect battery performance, in particular, capacity loss and voltage decay.¹⁶ These phase transitions have been reported to occur after delithiation,¹⁷ electrochemical cycling¹⁸ or by exposure to very high-density currents under the electron beam¹⁹. Thus, in this work, to monitor possible phase transitions and Mn migration, we have exposed the material to an electron beam dose of around $10^5 \frac{e}{\text{\AA}^2}$ per single image acquired (Figure 7). A careful observation of various regions along the surface of $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ shows significant differences. In particular, in some cases, the tetrahedral positions show brighter contrast than expected, when compared with computer simulations, which consider only Li in the tetrahedral positions.

To better understand this issue, three distinct regions were selected and highlighted by red, yellow and green diamonds (Figures 7a - c). These diamonds are rotated and magnified in the bottom part of the image to better illustrate the changes (Figures 7d - f). The colours have the following

meaning: (i) red diamonds represent no significant changes in contrast when compared with the computer simulations; (ii) green diamonds denote regions where enhanced contrast in the tetrahedral positions is observed for all images (ADF, dDPC, and iDPC), indicating the presence of Mn atoms, and (iii) yellow diamonds, which characterize areas where a brighter contrast is observed only for dDPC and iDPC images, thus implying the existence of very low substitutions of Mn for Li, which cannot be observed by ADF or HAADF. Such manganese migration to the tetrahedral positions has been previously reported [REF]. However, the amount of migration mentioned in these reports must be significantly higher in order for XRD or HAADF to detect it. Thus, our results indicate for the first time that dDPC and iDPC images can be used to detect very small amounts of Mn migration, even before cycling. In fact, Reed *et. al.*²⁰ showed by ab initio calculations that when Li vacancies are present, manganese migration is favourable in these structures.

In order to corroborate the process of Mn migration, computer simulation images were generated for different amounts of Mn substitutions for Li atoms in a tetrahedral position along one single atomic column, highlighted by the red circle in Figure 8. This model assumes 7 unit cells necessary to build an 8.34 nm crystal, in which the Li atoms in the tetrahedral positions were substituted by Mn atoms along one single atomic column. Both ADF and dDPC computed images are shown for different amounts of substitution, demonstrating the ability of the DPC technique to enhance the contrast associated with the presence of small amounts of Mn. It is evident that the use of DPC increases the relative intensities between heavier and lighter atomic columns, allowing the identification of small amounts of substitutions in the Li atomic column, which otherwise would not be identified by ADF, such as in the case of 2/14 substitutions (Figure 8b).

To better understand this behaviour, let us consider 1/14 substitutions as a function of thickness (Figure 9). The atomic model shown in Figures 9a was built, which shows the top and front view of a $2.5 \times 2.5 \times 8.34 \text{ nm}^3$ LiMn_2O_4 crystal, where one Li atom located at the topmost part of the model was substituted by a Mn atom. Figure 9b shows a simplified version of the model in Figure 9a, where only the Mn atoms are shown, to clearly observe the substitution, marked with the arrow. The images in Figures 9c to 9f display the ADF, iDPC, eDPC and dDPC simulations from top to bottom, for different thicknesses, 1, 3, 5 and 7 unit cells for Figure 9c, 9d, 9e and 9f, respectively.

These various thicknesses allow us to study the relative intensity between Mn atoms located in the octahedral (Mn_{oct}) and Mn located at the tetrahedral position (Mn_{tet}), $\text{Mn}_{\text{tet}}/\text{Mn}_{\text{oct}}$. Clearly, the ADF images in Figure 9c – 9f reveal a contrast dependence of this ratio, reducing the contrast of the substitution as the thickness increases. However, this evolution shows an opposite trend in DPC signals where the intensity ratio $\text{Mn}_{\text{tet}}/\text{Mn}_{\text{oct}}$ for eDPC, dDPC and iDPC signals maintain or increase as

the thickness increases (Figure S4). In other words, the ratio lower the number of substitutions, the greater the intensity ratio between the columns. This effect lowers the contrast at the tetrahedral sites where substitution occurs, thus preventing these columns from being noticed by the ADF and HAADF detectors.

Low Dose Experiments to Evaluate Mn Migration in Pristine $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$

Lower dose experiments were carried out to better control the kinetic energy transferred to the material and evaluate the evolution of the Mn migration. Figure 10a shows an ADF-STEM image of the surface of a pristine $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ particle, which was scanned for several frames to determine the substitution of Li atoms by Mn along the tetrahedral Li atomic columns. The results show, frame-by-frame, the appearance of Mn atoms in Li tetrahedral positions confirming previous findings at higher dose, using ADF, dDPC and iDPC (Figures 10b-e, 10f-l and 10j-m, respectively). The existence of Mn atoms in one of the tetrahedral positions is observed from the beginning of the image acquisition, as shown in Figure 10b and highlighted by the green arrow. The low concentration of Mn in this column prevents the observation with the ADF detector but it is clearly shown using dDPC (Figure 10f) and iDPC (Figure 10j). The yellow arrow in Figure 10b shows a Li atomic column in which Mn is not observed by any of the detectors in the initial frame, but it is evident in the final frame. As the number of the scanned frames increases from left to right, the total dose also increases, leading to the migration of Mn atoms to the Li column, highlighted by the yellow arrow.

These results corroborate the existence of low concentrations of Mn substitution in Li tetrahedral positions in $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$, which has been so far overlooked due to the fact that HAADF images are the typical images used to characterize these materials, and are not sensitive to a small number of substitutions. These results also help to elucidate previous reports where the Mn oxidation state has shown an evolution from the bulk to the surface in pristine $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$, revealing a more reduced Mn state on the surface of the particles.⁸ The substitution of Li atoms by Mn atoms at the surface was clearly observed. However, the origin of the reduction of the Mn oxidation state between the surface and the subsurface was not clear. This work may explain this fact as the existence of Mn migration into tetrahedral positions subsurface can reduce the overall oxidation state of Mn, leading to an intermediate state between the surface and bulk $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$.

Conclusions

In summary, we demonstrate that the DPC technique is capable of detecting low amounts of elemental substitutions, which help us understand the migration of species at atomic resolution. For

the case of $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$, there seems to be a low activation energy for Mn migration into the Li tetrahedral sites, which can be induced by the electron beam. Such migration can be monitored using atomic resolution DPC-STEM. The results also layout a new methodology to investigate the stability of Li-based compounds, by studying the migration of transition metals within the structure induced by the electron beam. This will allow, for instance, to determine the effect of compounds such as Ni, Co, to control the overall migration and structure.

Materials and methods

Sample preparation

Commercially available LiMn_2O_4 nanoparticles were suspended in water and dispersed by drop-casting method onto a lacey carbon grid (TED PELLA, INC.) for STEM and DPC imaging.

Scanning Transmission Electron Microscopy (STEM) Characterization

High angle annular dark-field (HAADF) STEM images were acquired on a double-corrected FEI Titan Themis operated at 200 kV. The images were recorded using a convergence angle of 15 mrad with a pixel dwell time set at 10 μs . A camera length of 91 mm was selected, which allows the HAADF detector to collect electrons between 94 and 200 mrad.

Differential phase contrast (DPC-STEM) characterization

The differential phase-contrast images were acquired using a four segmented annular detector (DF4), coupled to a double-corrected FEI Titan-Themis microscope operated at 200kV. Images from individual segments were acquired with a pixel dwell time set at 4 μs using a 228 mm camera length, resulting in acceptance angles between 9 – 51 mrad, while when collecting simultaneously the signal from DF4 and annular dark field (ADF), the acceptance angles were limited to 9-36 mrad and 36 – 176, respectively. The DPC technique was used to image the in-plane displacement of the transmitted electrons, and the images proportional to the projected potential,¹ the projected electric field^{3 4} and the projected charge distribution⁵ were calculated according to the references. The images presented in the manuscript were acquired using an experimental electron dose about $10^5 \frac{e}{\text{\AA}^2}$. Additionally, lower dose experiments were performed at doses of about $10^3 \frac{e}{\text{\AA}^2}$.

Multisliced image simulations

Simulated HAADF, ADF, ABF and DPC-STEM images, were carried out using Dr. Probe V1.9 software package,²¹ using a LiMn_2O_4 spinel structure oriented in [011] direction. The thickness of the model varied from 0 – 8.34 nm. Frozen-lattice configuration was used and the simulations were carried out

reproducing the experimental conditions at 200 kV and 15 mrad aperture. Additionally, simulations of LiMn_2O_4 structure in which Mn substitutes Li atoms in a particular Li atomic column were carried out. The number of substitutions considered was 1, 2, 4, 6 and 10 atoms in one Li atomic column. The images proportional to the projected potential, the projected electric field, and the projected charge distribution, were calculated according to the references^{2 3 4 5}.

DFT simulations

Density Functional Theory (DFT) calculations were performed using the open source suite Quantum ESPRESSO^{22,23}. The exchange-correlation functional was the generalized gradient approximation of Perdew-Burke-Ernzerhof²⁴ (GGA-PBE) and ultrasoft full relativistic pseudopotentials were used.

The energy cutoff was 120 Ry and for the integration over the Brillouin-zone a Monkhorst-Pack²⁵ sampling with 7 x 7 x 7 points was used. To have a more accurate potential near the center of each atom, the pseudopotential region was substituted by the atomic potential after the DFT calculations.

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