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Comprehensive analysis of TEM methods for $LiFePO_4/FePO_4$ phase mapping: spectroscopic techniques (EFTEM, STEM-EELS) and STEM diffraction techniques (ACOM-TEM)

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ABSTRACT

Transmission electron microscopy (TEM) has been used intensively in investigating battery materials, e.g. to obtain phase maps of partially (dis)charged (lithium) iron phosphate (LFP/FP), which is one of the most promising cathode material for next generation lithium ion (Li-ion) batteries. Due to the weak interaction between Li atoms and fast electrons, mapping of the Li distribution is not straightforward. In this work, we revisited the issue of TEM measurements of Li distribution maps for LFP/FP. Different TEM techniques, including spectroscopic techniques (energy filtered (EF)TEM in the energy range from low-loss to core-loss) and a STEM diffraction technique (automated crystal orientation mapping (ACOM)), were applied to map the lithiation of the same location in the same sample. This enabled a direct comparison of the results. The maps obtained by all methods showed excellent agreement with each other. Because of the strong difference in the imaging mechanisms, it proves the reliability of both the spectroscopic and STEM diffraction phase mapping. A comprehensive comparison of all methods is given in terms of information content, dose level, acquisition time and signal quality. The latter three are crucial for the design of in-situ experiments with beam sensitive Li-ion battery materials. Furthermore, we demonstrated the power of STEM diffraction (ACOM-STEM) providing additional crystallographic information, which can be analyzed to gain a deeper understanding of the LFP/FP interface properties such as statistical information on phase boundary orientation and misorientation between domains.

1. Introduction

Lithium (Li) batteries have been developed for more than two decades. They have plenty of commercial applications, which strongly impact human life. Lithium iron phosphate ($LiFePO_4$) is one of the most promising cathode materials for the upcoming next generation of Li ion batteries and has attracted great attention. Understanding the microscopic mechanism of the de/lithiation processes during electrical cycling is crucial to improve the performance of this material. Efforts to experimentally detect the lithium distribution in partially charged/discharged states at nanoscale resolution are therefore essential. Many advanced techniques have been developed to obtain Li distribution maps: Scanning transmission X-ray microscopy (STXM) [1,2] or ptychography techniques [3–5] in synchrotron based setups were used to observe de/lithiation phase boundaries that started the discussion around its relationship to cycling current; Electron back scatter diffraction (EBSD) techniques in a scanning electron microscope (SEM) [6] was used to investigate the influence of the distance of particles to current collectors for the de/lithiation process.

Transmission electron microscopy (TEM) offers various sophisticated methods for $LiFePO_4/FePO_4$ (LFP/FP) phase mapping with high spatial resolution [6–16]. The mapping methods can be sorted into two families: one are spectroscopy methods based on the chemical information encoded in the energy spectra; the other are diffraction methods relying on the crystallographic information recorded in diffraction patterns or high resolution (HR)TEM images. In the first family of methods, electron energy loss spectroscopy (EELS) was one of the forerunners to investigate the Fe-L and O-K edges, Li-K and Fe-M edges as well as the low-loss range

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resulting from interband transitions and plasm resonances [7,9,17–19]. The approach has been extended to 2 dimensions by combining EELS with scanning transmission electron microscopy (STEM) to obtain STEM-EELS spectral imaging (SI) and, for example, the differences in the O-K and Fe-L core loss spectra in LFP/FP have been used for phase mapping [8]. Alternatively, 2D phase mapping has been implemented by energy filtered transmission electron microscopy (EFTEM) spectral imaging, where the phase has been determined by measuring the chemical shift of the Fe-L_3 edge between the LFP and FP phases [11]. In the second family of methods, detection of the difference in lattice constants between LFP and FP has been adopted in the TEM to distinguish the phases. High resolution TEM imaging (HRTEM) and selected area electron diffraction (SAED) were applied to study the de/lithiation processes [13–16]. However, HRTEM provides only limited statistical information because of the small field of view. Automated crystal orientation mapping inside the TEM (ACOM-TEM), which was originally developed for orientation analysis of nanocrystalline and ultrafine grained materials [20,21], has been used to obtain LFP/FP phase maps over micrometers with a high spatial resolution of 1-2 nm [12].

While the different spectroscopic and diffraction techniques have been applied to study the phase distribution in LFP/FP, so far, there is no convincing evidence indicating full agreement between the chemical information and the crystallographic information based phase maps because of a lack of comparison between the results gained from the two types of methods. In particular, the conclusions deduced from the STEM-EELS results by Honda et al. [8], where a core-shell FP/LFP de/lithiation structure was observed, is in discrepancy to the observation from the ACOM-TEM work from Brunetti et al. [12], where a Domino-Cascade model (de/lithiating particle by particle) was confirmed. The limited reliability of EFTEM based phase maps for samples with varying thickness has already been discussed by Sugar et al. [11], whereas for diffraction based analysis, questions about the reliability arise due to the structural similarity of both phases and the corresponding small difference between the LFP and FP lattice constants, especially for higher index orientations. Therefore, in this work, we revisited the issue of TEM measurements of Li distribution maps for LFP/FP. We applied the different TEM techniques, including EFTEM-SI in the energy range from low-loss (interband transition, volume plasmon) to core-loss (Li-K and Fe-M edges, Fe-L edge) and ACOM-TEM for lithiation mapping of the same sample and sample location. This enabled a direct comparison of the results and, because of the strong difference in the detection process, provides a good measure for the reliability of the analysis. The maps obtained by all methods showed excellent agreements with each other, for ultra-microtomed sample with uniform thickness, proving the reliability of both the EFTEM/STEM-EELS maps (chemical information) and ACOM-TEM phase maps (crystallographic information). A comprehensive comparison of all methods was given in terms of information content, dose level, acquisition time and signal quality. The latter three are crucial for the design of in-situ experiments with beam sensitive Li-ion battery materials. Furthermore, we demonstrated the power of ACOM-TEM with the additional crystallographic information, which can be analyzed to gain a deeper understanding of the LFP/FP interphase properties such as statistical information on phase boundary orientation and misorientation between domains.

2. Experimental

2.1. Sample preparation

The electrode was prepared by mixing LFP nanoparticles with Super P carbon black and binder. The electrode was first charged to 4.0 V at 2 mA (ca. 1 C rate). It was then discharged for 30 min at 2 mA to reach ca. 50% lithiation state. In this state, the electrode was dismounted from the cell for further TEM specimen preparation.

Misleading results of EFTEM-SI can be caused by thick specimens. Therefore, in this work, we used ultramicrotomy for the sample preparation. Details are given in the supplementary information Section 1 (SI.1). The average thickness of the active material (LFP/FP particles) in the specimen was measured by EFTEM thickness mapping to be around 0.6λ (Fig. S 1) corresponding to $\sim$80 nm.

2.2. ACOM-TEM

ACOM-TEM data was collected on a Tecnai F20 (Philips) operated at 200 kV in micro-probe STEM mode and equipped with a NanoMegas ASTAR system. For the data acquisition, spot size 8, gun lens 6, extraction voltage of 4.5 kV and 30 μm condenser (C2) aperture were used. The probe size was around 1.0–1.5 nm diameter with a convergence semi-angle of 0.8 mrad. The camera readout frequency was set to 100 fps (frames per second) for the diffraction pattern acquisition. The camera length was set to 100 mm. To minimize the influence of dynamic scattering, the electron beam was precessed with a precession angle of 0.5°, which slightly broadened the beam. The size of the final electron probe was around 3 nm. The step size for the ACOM-TEM image acquisition was 6 nm, the frame size 488 × 590 pixels, in order to reach a large mapping area comparable to the EFTEM-SI mapping. Fig. S 2a shows an example of a nano beam electron diffraction pattern from the ACOM-TEM data used in the current work. The small diffraction disks are the results of the convergence angle setup of the electron beam for nano beam diffraction. Matching of experimental diffraction pattern and simulated diffraction templates for the determination of crystal orientation and phase identification has been computed using the ACOM-TEM NanoMegas software package. The banks (database) of the diffraction templates have been calculated based on the olivine-type LFP and FP crystal structures with the axes defined as $a = 10.329$ Å, $b = 6.006$ Å and $c = 4.691$ Å for LFP and $a = 9.814$ Å, $b = 5.789$ Å and $c = 4.782$ Å for FP [22]. More details for the templates matching are described in the supplementary information Section 2 (SI.2). The final orientation and phase data were imported into matlab and analyzed using MTEX 4.1 [23] for quantification of the misorientation and orientation density.

2.3. EFTEM-SI

EFTEM-SI and STEM-EELS-SI data for determining the LFP/FP phase maps were acquired using an aberration (image) corrected Titan 80–300 (FEI Company) operated at 300 kV, equipped with a GIF tridium spectrometer with a BM-UltraScan CCD camera. For the acquisition of the EFTEM-SI, a μp EFTEM setup was used with a frame size of 512 × 512 pixels and a pixel size of 6.13 nm. To determine the LFP and FP phases, two different regimes for the EFTEM-SI are available: at high energy loss, i.e. Fe-L_3 edge with an onset at 708 eV, and at low energy loss from 0 to 75 eV including interband transitions (4–20 eV), volume plasmon (20–30 eV) and Li-K/Fe-M edge (55 to 70 eV). For the acquisition of the Fe-$L_{3,2}$ edges, we adopted the settings suggested by Sugar et al. [11]. As measuring condition a 4 eV energy slit and an energy shift step of $\Delta E = 1$ eV per image with an exposure time of 120 s per image were applied. The energy range was set from 696 eV to 735 eV (40 images). A 40 μm objective aperture was selected. In case of the low-loss regime, a 1 eV energy slit and a shift step of $\Delta E = 0.5$ eV per image were applied. The acquired energy range was from