

Comparison of energy filtered TEM spectra image and automated crystal orientation mapping in $\text{LiFePO}_4/\text{FePO}_4$ phase mapping

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Lithium iron phosphate (LiFePO_4 , LFP) is one of the most promising cathode materials for the next generation of Li ion batteries and attracts great attentions. Experimental mapping the lithiated (LFP) and delithiated phase (FePO_4 , FP) at nanoscale resolution provides knowledge on the microscopic mechanism of the reaction processes during electrical cycling, which is crucial to improve the limits of this material. Versatile scanning / transmission electron microscopy (S/TEM) techniques, due to the advantage of intrinsic imaging ability by the electron optics, have attracted extreme interest in high resolution phase mapping. The methods are generally sorted into two kinds: one is based on electron energy loss spectroscopy (EELS), such as energy filtered TEM (EFTEM) [1], relying on the chemical information in the energy spectra; the other is automated crystal orientation mapping (ACOM) [2], originally designed for orientation analysis of nanocrystalline materials [3], relying on the crystallographic information recorded in diffraction patterns. However, so far, there is no strongly convincing evidence indicating the consistency between the chemical and the crystallographic information in the phase map, because of lacking comparison of the results between the two kind methods.

In this work, we applied both EFTEM and ACOM methods to the same part of a sample (half lithiated) for comparison. Maps obtained by ACOM and EFTEM of Fe- $L_{3,2}$ (figure 1 a, b) show excellent agreements with each other. It proves the reliability of both methods, i.e. the consistence of the chemical and crystallographic information for the LFP/FP system. Furthermore, we demonstrate that the properties of the LFP/FP interfaces can be further characterized from the crystallographic data obtained by ACOM: on average 1.4° misorientation was observed at all interfaces (figure 1 d, e), and these interfaces have a preferred orientation with the normal close to the a-axis (100), but slightly deviated towards the c-axis (001) (figure 1 f, g) in agreement with [4]. Further attention is drawn to the low energy loss regime for EFTEM analysis. Figure 2 a, c and e respectively shows a map measured from the Li-K & Fe-M edges (figure 2 b), and mapping of the dielectric function (figure 2 d) and the volume plasmon center (figure 2 f). Finally, a comprehensive comparison of all methods is given in terms of information contents, dose level, acquisition time and signal quality. The latter three are crucial for the design of in-situ experiments [5].

References:

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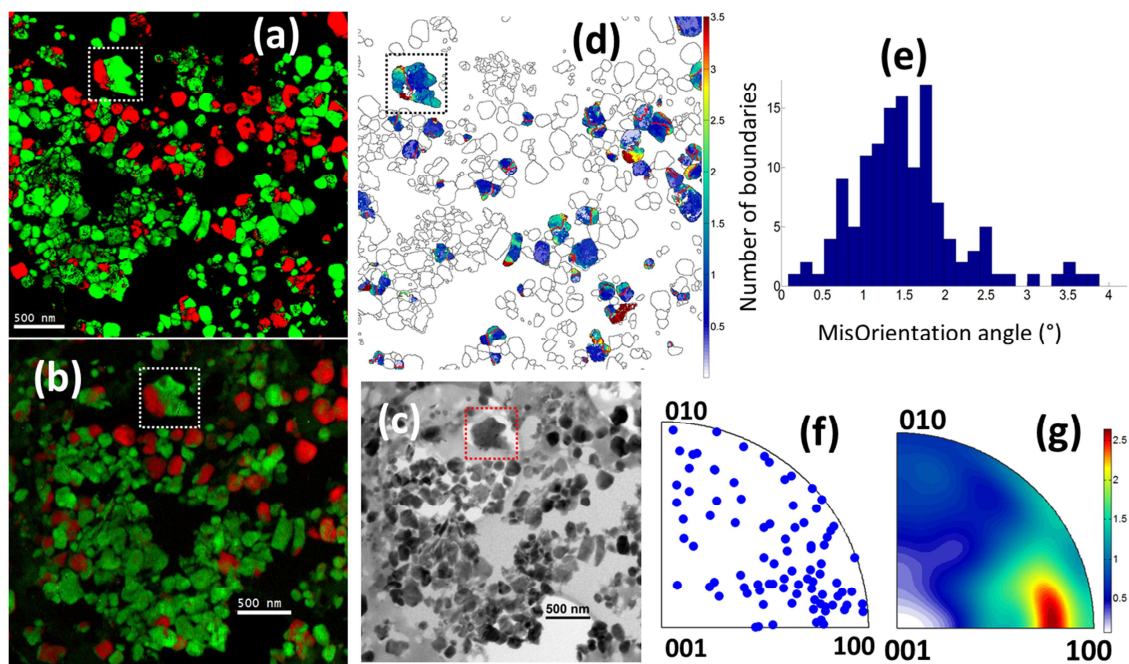


Figure 1. LFP(green)/FP(red) maps by (a) ACOM, (b) EFTEM-SI Fe-L₃. (c) Bright-field image as reference. Information abstracted from ACOM data: (d) Misorientation map, color on each pixel corresponds to a misorientation angle between the orientation on that pixel and mean orientation in the particle. (e) Angular distribution of the misorientations. (f) Inverse pole figure of the orientations of the LFP/FP interfaces in 88 populations. (g) The orientation density (ODF) calculated from f.

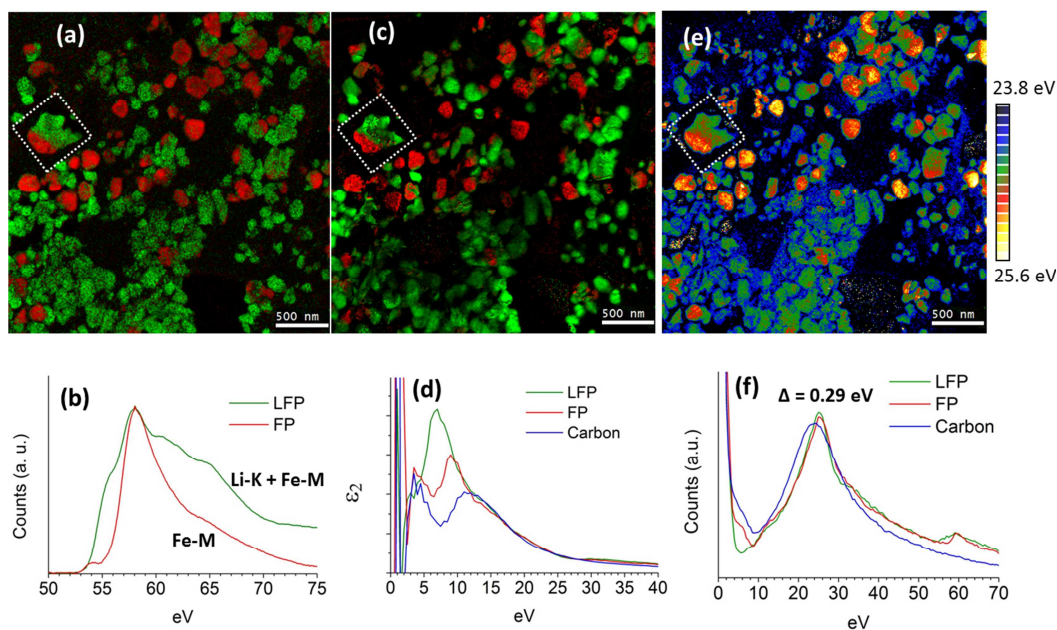


Figure 2. EFTEM phase maps (a) from Li-K & Fe-M signals in (b), (c) according to the dielectric functions shown in (d) computed by Kramers-Kronig equation from the signal caused by interband transitions. (h) Volume plasma center map. (i) low-loss spectra of LFP, FP and carbon substance.