Domain structure in Delithiated $LiFePO_4$, a cathode material for Li ion Battery Applications

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Delithiation is a basic step in the operation of the Li ion battery and it involves the extraction of Li ions from the lattice of the cathode material and insertion into the lattice of the anode. $LiFePO_4$ is a cathode material whose wide application in high energy Li ion batteries, is limited by low ion and electron diffusion [1]. Partially delithiated $LiFePO_4$ grains are known to exist in a two phase state characterized by the delithiated, $Li_{1-x}FePO_4$ and lithiated $LiFePO_4$ phases. It has been proposed that poor mobility of Li ions across the interface between these two phases plays an important role in limiting Li diffusion within the $LiFePO_4$ grain [3]. Therefore, investigating the two-phase domains in $LiFePO_4$ is a crucial step towards a better understanding of the Li diffusion in $LiFePO_4$.

We have studied the phase structure in partially delithiated $LiFePO_4$ grains using Geometrical Phase Analysis (GPA) method [4, 5]. In a distorted lattice, quantitative information regarding structural deformations can be obtained from the phase changes of the Fourier coefficients $\boldsymbol{g_i}$ in the corresponding HRTEM image. In the absence of structural distortions, the phase of $\boldsymbol{g}$-component is constant, while in a distorted lattice the phase is modified by the displacement field $\boldsymbol{u(x, y)}$; the phase is then $\boldsymbol{-2\pi g.u(x, y)}$. In the resulting phase map, the intensity at a point is then proportional to the displacement. All HRTEM images were obtained using the Cs corrected Titan 80-300kV microscope. Figure 1 shows the bright field image of a partially delithiated $LiFePO_4$ grain. Figure 1(b) shows the HRTEM image used to determine the structural variations along the Li diffusion paths in the [010] direction. The amplitude image in Figure 1(c) shows the changes in intensity. Figure (d) shows the changes in the phase along the [010] direction. The contrast changes in the phase image represent a phase shift of $\boldsymbol{\pi}$ between the regions with dark and bright contrast. This is a result of atomic plane rearrangement and lattice parameter variation along the Li ion diffusion path. We will discuss these results in the context of the methods applied, $LiFePO_4$ phase transitions and Li ion diffusion during Li battery operations.

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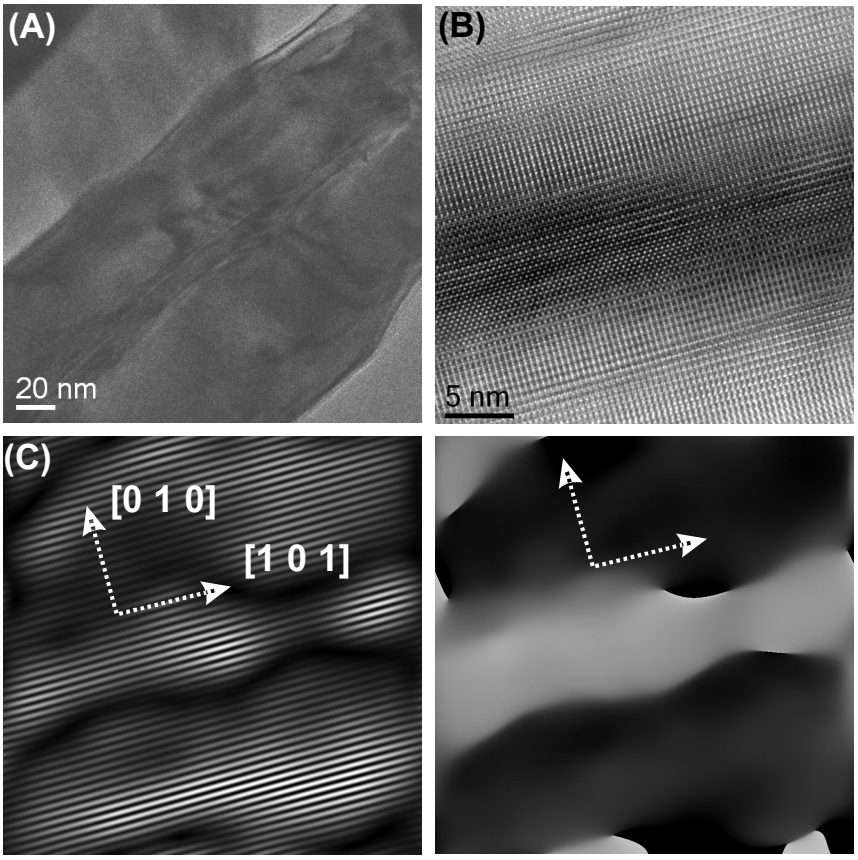

Figure 1: GPA analysis of delithiated LiFePO4 grains. (a) A bright field image showing the domain morphology (b) the corresponding HRTEM image (c) Amplitude image showing intensity changes along [010] (d) phase image showing the phase changes along [010] direction.