Phase boundaries in the delithiated $LiFePO_4$ crystals

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Introduction Rechargeable lithium ion battery[1)] (LIB) has a large global market and commercially used as a power source for portable devices, due to its high energy density. Furthermore, in recent years, it is highly warranted to expand its usage to large-scale devices such as rechargeable batteries for electric vehicles. From the material design viewpoints, it is important to understand the lithium and electron transport mechanisms in cathode/anode materials and electrolytes.

$LiFePO_4$ is one of the most promising cathode materials due to its high theoretical electric capacity, high-temperature stability, and good cyclic performance[2)]. Previous studies have shown that lithium insertion/extraction in $LiFePO_4$ occurs by two-phase process[3)]. In other words, $LiFePO_4$/$FePO_4$ interfaces propagate through the bulk region with inserting/extracting lithium and electrons cooperatively. Although this two-phase mechanism obviously dominates entire battery properties, neither atomic-scale structures at the interface nor diffusion processes lithium and electron has been understood in detail. In this study, transmission electron microscopy (TEM) observations have been performed to characterize the two-phase interfaces.

Experimental method

Pristine $LiFePO_4$ was fabricated by solid state reaction. The specimen was then partially delithiated by NO_2BF_4 (Nitronium tetrafluoroborate) in acetonitrile solvent. XRD analysis of partially delithiated sample have confirmed that $LiFePO_4$ (LFP) and $FePO_4$ (FP) phases coexist and there is no detectable third phase. Subsequently, TEM and STEM (scanning TEM) observations have been performed to identify LFP/FP interfaces within each particle. In this study, conventional bright- and dark-field imaging techniques were also used to determine LFP or FP phase of relatively large and thick particles.

Results and Discussion

Figure 1 (a) and (b) shows a bright-field image (BF) of delithiated particle, and its diffraction pattern (DP). There is a clear contrast inside the particle, which must represent LFP/FP interfaces in this particle (Fig.1 (a)). Furthermore, DP shows peak splits which stem from different lattice constants of two phases (LFP : a=10.329 Å, b=6.007 Å, c=4.691 Å / FP : a=9.81 Å, b=5.79 Å, c=4.78 Å. See inset in Fig.1 (b)), also supporting the existence of two phases. From DP, it can be seen that two phases are slightly tilted relative to one another. Fig.1 (c) shows a dark-field image (DF) of the same particle. Various images were taken from different direction to identify lattice defects such as misfit-dislocations at LFP/FP interfaces in this study. High density of complicated contrast has been observed in the middle part but not in the right and left side. This indicates that high density of lattice defects such as dislocation may be introduced in the middle part and lithium is not homogeneously distributed within the region.

High-resolution observations were also performed for single phase LFP images shown here. Figure 2 (a) and (b) show HAADF-STEM images along *b* and *c* crystal axis. Since HAADF imaging is less sensitive to low atomic-number (Z) elements such as lithium and oxygen, only iron and phosphorus columns have been observed. We are currently performing annular bright-field (ABF) STEM observations[4) 5)], which is sensitive to low-Z elements, for visualizing lithium and oxygen.

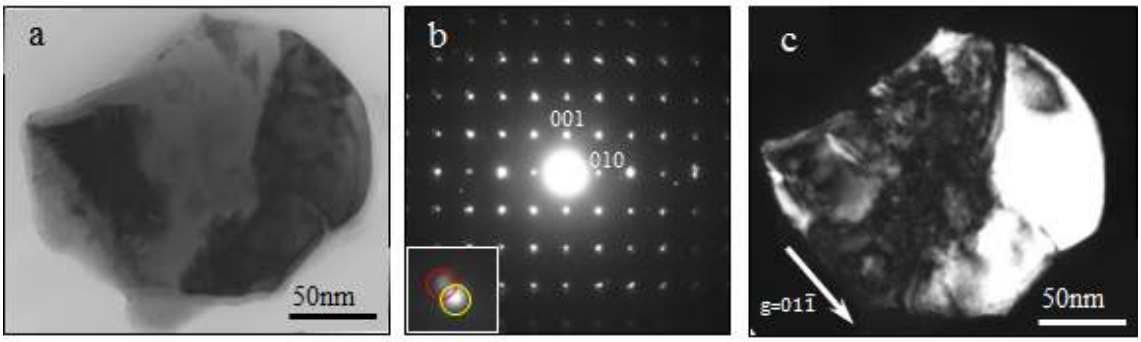

Fig. 1
(a) A bright-field image of $Li_{0.6}FePO_4$ particle.
(b) A zone-axis diffraction pattern (100 direction) which shows spot-splits.
(inset) A magnified $0\bar{3}2$ spot. Yellow and red circles represent LFP and FP spot, respectively.
(c) A dark-field image taken from the same particle of (a).

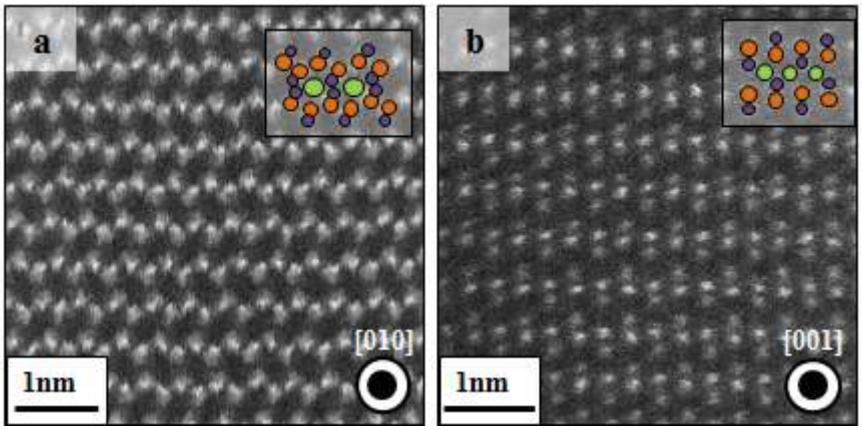

Fig.2 HAADF-STEM images of LFP single phase along (a) b-axis and (b) c-axis directions. (insets) Schematic views of atomic configurations. Green, purple and brown circles represent Li, P and Fe atoms, respectively. Oxygen atoms are not shown in these figures.

References

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