

In Situ Observation of Structural Change in Single-Crystalline LiFePO₄ Nanoflakes during Electrochemical Cycling

Sungkyu Kim¹, Vinayak P. Dravid¹ and Kai He¹

¹ Department of Materials Science and Engineering and NUANCE Center, Northwestern University, Evanston, Illinois 60208, United States

Lithium iron phosphate (LiFePO₄) has been demonstrated as a commercially important cathode material for lithium-ion batteries due to its large theoretical capacity (~170 mAh/g), superior stability and cyclability [1]. Theoretically, LiFePO₄ and FePO₄ are the only two stable phases in bulk equilibrium condition, indicating that interfaces exist between these two phases during lithiation and delithiation processes. However, for high-rate battery applications, size reduction, carbon coating and doping are essential modifications to improve their low ionic and electronic conductivities. Among various methods, reducing the size to nanoscale can effectively lead to increase of reaction rate and meanwhile may modify the reaction mechanisms [2]. Although enormous studies of nanosized LiFePO₄/FePO₄ have been reported, the phase transformation through either solid-solution or two-phase mode still remains elusive [3, 4]. Here, we report the structural change in LiFePO₄ nanoflakes during reversible electrochemical reactions using in situ transmission electron microscopy (TEM) techniques.

Figure 1a and b show TEM images of [100]-oriented single-crystalline LiFePO₄ nanoflake with orthorhombic structure and typical size of 170 nm × 300 nm (*b* × *c*). The dimension of *a*-axis has ultra-thin thickness (<20 nm) compared to the *bc* plane, as shown in Figure 1c and d. The [100] direction has been typically considered to be difficult for migration of Li⁺ [5], therefore, the unique geometry of ultra-thin nanoflake provides an excellent model system to investigate the Li⁺ diffusion along *b* and *c* axes, and further unveil the dynamic LiFePO₄/FePO₄ phase transitions in real time. The nanoflakes were mounted on the Au grid with ultra-thin carbon films, which was electrically bonded to a metal wire as the cathode; while a piezo-driven probe with lithium-coated tip serves as the counter electrode, as shown in the schematics in Figure 1e. Figure 1f shows scanning TEM (STEM) image of a few nanoflakes after the first delithiation process, which shows the same shape without noticeable size change compared to the pristine state. However, subsequent lithiation and delithiation cycles showed reversible areal expansion and contraction in excess of the theoretical 7% volume difference between the LiFePO₄ and FePO₄ crystalline phases. After multiple cycles, the final area could not return to its original state, indicating that additional structural change and intermediate Li_xFePO₄ phase may occur during electrochemical cycling. Using in situ selected area electron diffraction (SAED), we found that the crystalline structure was maintained during the first delithiation process (Figure 2b and c). In contrast, obvious structural change occurred during the lithiation process (Figure 2d–f), where SAED spots gradually disappeared as Li⁺ inserted into Li_xFePO₄ lattice. After the lithiation process, only a few diffraction spots remained along with broadened rings, implying that LiFePO₄ was changed to an intermediate state with amorphous-like structure. Combining in situ STEM and SAED results, we demonstrate that the reversible electrochemical reactions involve volume changes caused by intermediate phase, which needs further clarification to show valuable insights into understanding the phase transformation mechanism in LiFePO₄ [6].

References:

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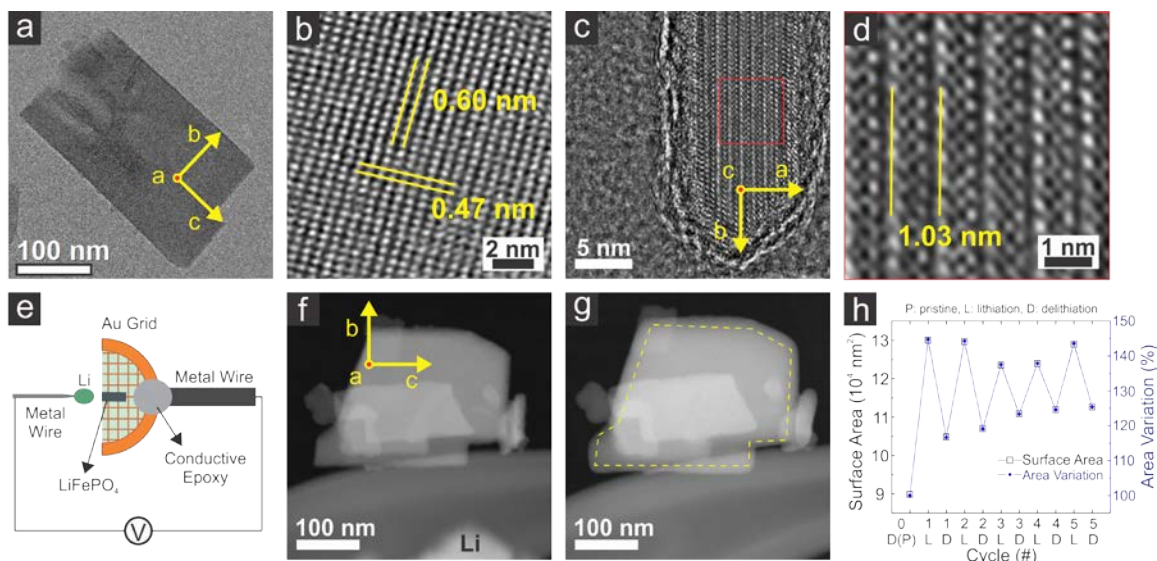


Figure 1. (a) TEM and (b) High resolution TEM (HRTEM) images of the pristine LiFePO₄ nanoflake. (c) HRTEM image of the vertically positioned nanoflake and (d) magnified image of the red square. (e) Schematic illustration of the in situ experiment setup. STEM images of (f) before the first lithiation process and (g) after the last delithiation process. The yellow dotted line indicates the shape of the nanoflake in (f). (h) Areal variation during electrochemical cycling.

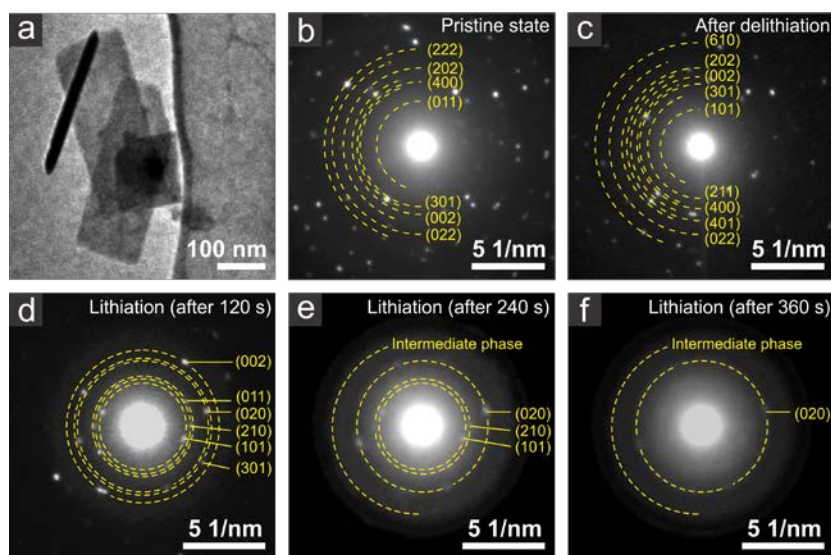


Figure 2. (a) TEM image of LiFePO₄ nanoflakes. (b) Initial SAED pattern obtained from (a). (c) SAED pattern after the first delithiation process. (d-f) Sequential snapshot images of SAED patterns during the subsequent lithiation process.