

Rate-dependent Reversal of Lithium Concentration During Intercalation into Li_xFePO_4 Nanoparticles

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Electrochemical reactions in most commercial battery electrodes take place through an intercalation process, during which lithium ions are inserted into interstitial sites of the host without causing significant structural changes in the electrodes [1]. LiFePO_4 (LFP) is one typical intercalation-type cathode known for its superior safety and cycling stability. Especially, nanoparticulate LFP has unique advantages over their microparticulate counterparts, and has been extensively investigated over the last decade [2]. However, the origin of high-rate capability in nanoparticulate LFP has been a subject of debate, since it is in conflict against the common belief of a sluggish two-phase transformation process in this material [3]. Recent atomistic calculations predicted a single-phase solid-solution transformation during fast lithiation of nano-sized LFP, which provided the first explanation for the high-rate capability [4]. Solid-solution transformation was identified through fast *in situ* X-ray diffraction (XRD) measurements [5]. Yet, how Li intercalation occurs locally in a single LFP nanoparticle remains unresolved since *real-time* observation at such a fine scale is still lacking. High-resolution transmission electron microscopy (HRTEM) is capable of exceptional spatial resolution, and it has recently been developed for *in situ* tracking of the phase evolution [6,7]. However, without the formation of distinctive phase boundaries during a monophasic solid-solution transformation in Li_xFePO_4 , the subtle change in lattice spacing, at sub- \AA scale, cannot be directly resolved by *in situ* HRTEM [6].

Herein, we report advancement in *in situ* techniques enabling *real-time* tracking of lithium intercalation in a single nanoparticle at different rates. Geometric phase analysis (GPA) was developed for processing time- and position- resolved lattice images, allowing for direct correlation of local displacement with the Li concentration within a single solid-solution phase. Therefore, this method enables real-time visualization of the evolution of local Li concentration within a single nanoparticle. Inhomogeneous solid-solution transformation within a single nanoparticle was revealed *via* this new approach and *in situ* electron diffraction, accompanied with an unexpected reversal of local lithium concentration at the nanometer scale (Figure 1). The amplitude of concentration reversal is rate dependent, and when the lithiation rate was reduced, the amplitude decreased (Figure 2). Phase-field simulations indicated that the presence of spatially varying chemical potential functions within the nanoparticle would lead to such concentration reversal (Figure 2E). The variation in chemical potential functions may be caused by the formation of anti-site defects; at a lower rate, it is reasonable to expect fewer defect formation, which could explain why the amplitude of concentration reversal reduces at lower lithiation rates. The findings provide new insights into the correlation between local dynamics of defects and *non-equilibrium* electrochemical reactions within individual intercalation-type particles.

References:

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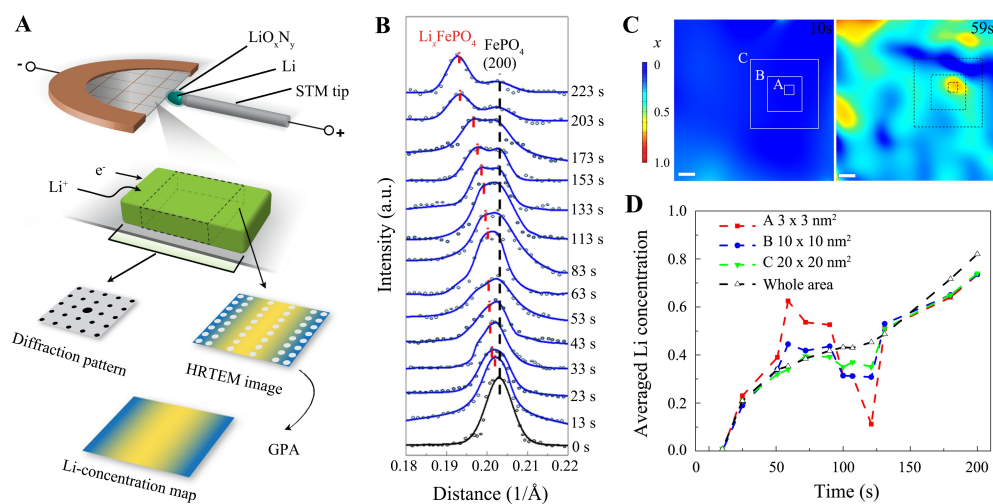


Figure 1. Lithium concentration evolution within a single Li_xFePO_4 nanoparticle during lithiation. (A) Electrochemical cell enabling *in situ* electron diffraction and HRTEM measurements in single particles. The HRTEM imaging coupled with GPA generates the spatial distribution of Li concentration in local areas of single particles. (B) Solid solution transformation revealed by the evolution of intensity profiles of the (200) diffraction spots. (C) 2D maps of local Li concentration at different states during lithiation at 18 C. Color scale indicates normalized Li concentration x . Scale bar: 5 nm. (D) Evolution of Li concentration averaged over different areas (as marked by squares in C). Reproduced from Ref. 8.

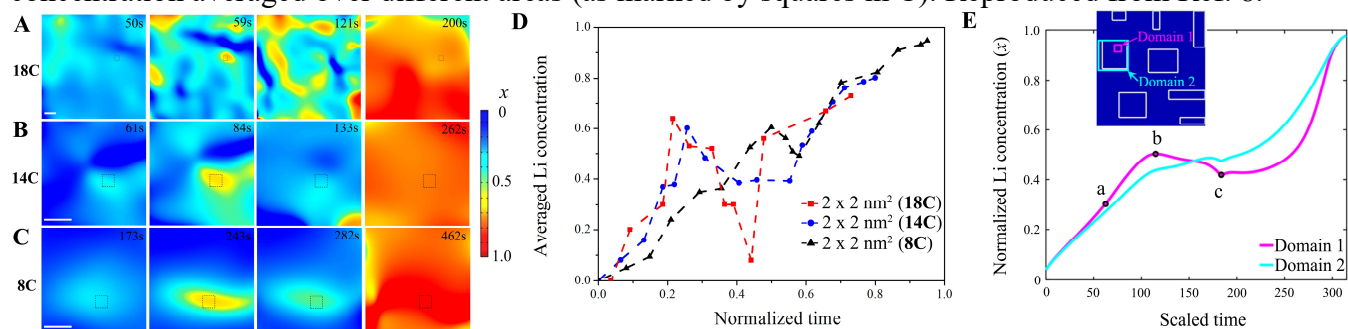


Figure 2. Concentration reversal at different rates. (A-C) Typical concentration maps at rates of 18C, 14C, 8C respectively. Scale bars: 5 nm. (D) Evolution of local Li concentration at different rates, averaged over the area with the same size (marked by black boxes in A-C). (E) Simulated evolution of Li concentration over domains 1, 2 in the inset. The domains possess different chemical potential functions. The concentration in domain 1 increases from point a to b, and then decreases until point c.