# Atomic-Level Real-Time Observation of Crystal Growth and Evaporation in $LiFePO_4$ at High Temperature

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When crystalline particles are dispersed in their matrix, such as a solution or vapor, it is readily observed that particles larger than those of average size grow, accompanying the dissolution of smaller particles into the matrix at the same time. This particle coarsening process has generally been referred to as Ostwald ripening. As the physical properties of crystals significantly vary with their ultimate size and shape,[1] observation and appropriate control of their growth and dissolution behavior during the ripening process have been recognized as important issues in crystallization studies over the past several decades.

Recent advances in transmission electron microscopy (TEM) enable atomic-scale imaging in Li intercalation compounds for direct visualization of lattice defects, phase transition, and structural evolution.[2–9] In particular, a variety of techniques have been utilized for real-time observations in TEM, providing unexpected and new experimental findings.[10–13] Using *in situ* high-resolution electron microscopy (HREM) with a heating specimen holder, in this study we demonstrate, for the first time, the atomic-level evaporation behavior of $LiFePO_4$ crystals in real time at high temperature (Figure 1).[14] Prior to detailed observation of crystal evaporation, we also investigated the growth behavior of atomically flat low-index surfaces. A systematic comparison with image simulations along with density-functional theory calculations demonstrated that the cations evaporate preferentially over the $[PO_4]^{3-}$ oxyanions, accompanying fast charge transfer from the nearest-neighboring Fe and O. The present study thus shows that our combined technique based on high-temperature HREM and systematic image simulations is a powerful tool to understand the dynamic characteristics of crystal growth and evaporation.

## References

1. C. Burda, X. Chen, R. Narayanan, M. A. El-Sayed, *Chem. Rev.*, **105**, 1025 (2005).
2. S.-Y. Chung, S.-Y. Choi, T. Yamamoto, Y. Ikuhara, *Phys. Rev. Lett.* **100**, 125502 (2008).
2. S.-Y. Chung, S.-Y. Choi, T. Yamamoto, Y. Ikuhara, *Angew. Chem. Int. Ed.* **48**, 543 (2009).
3. S.-Y. Chung. Y.-M. Kim, S.-Y. Choi, *Adv. Funct. Mater.* **20**, 4219 (2010).
4. B. Xu, C. R. Fell, M. Chi, Y. S. Meng, *Energy Environ. Sci.* **4**, 2223 (2011).
5. S.-Y. Chung. J.-G. Kim, Y.-M. Kim, Y.-B. Lee, *Adv. Mater.* **23**, 1398 (2011).
6. K. A. Jarvis, Z. Deng, L. F. Allard, A. Manthiram, P. J. Ferreira, *Chem. Mater.* **23**, 3614 (2011).
7. S.-Y. Chung, S.-Y. Choi, S. Lee, Y. Ikuhara, *Phys. Rev. Lett.* **108**, 195501 (2012).
8. S.-Y. Chung *et al.*, *Nano Lett.* **12**, 3068 (2012).
9. M. Gu *et al.*, *Nano Lett.* **12**, 5186 (2012).
10. S.-Y. Chung, Y.-M. Kim, J.-G. Kim, Y.-J. Kim, *Nature Phys.* **5**, 68 (2009).
11. J. Y. Huang *et al.*, *Science* **330**, 1515 (2010).
12. C.-M. Wang *et al.*, *Nano Lett.* **11**, 1874 (2011).
13. F. Wang *et al.*, *Nature Commun*. **3**, 1201 (doi : 10.1038/ncomms2185) (2012)
14. S.-Y. Chung, Y.-M. Kim, S.-Y. Choi, J.-G. Kim, *J. Am. Chem. Soc.* (in press).

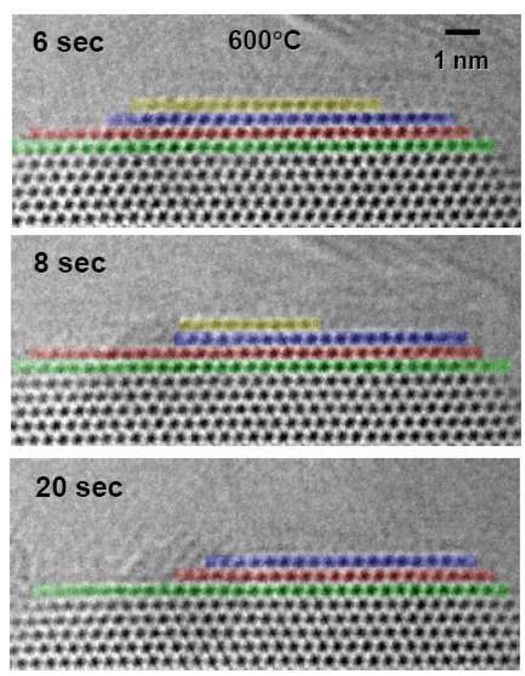


**Figure 1**. A series of *in situ* HREM images of a shrinking $LiFePO_4$ crystal at 600°C.