Supporting Information

***In operando* observation of temperature-dependent phase evolution in lithium-incorporation olivine cathode**

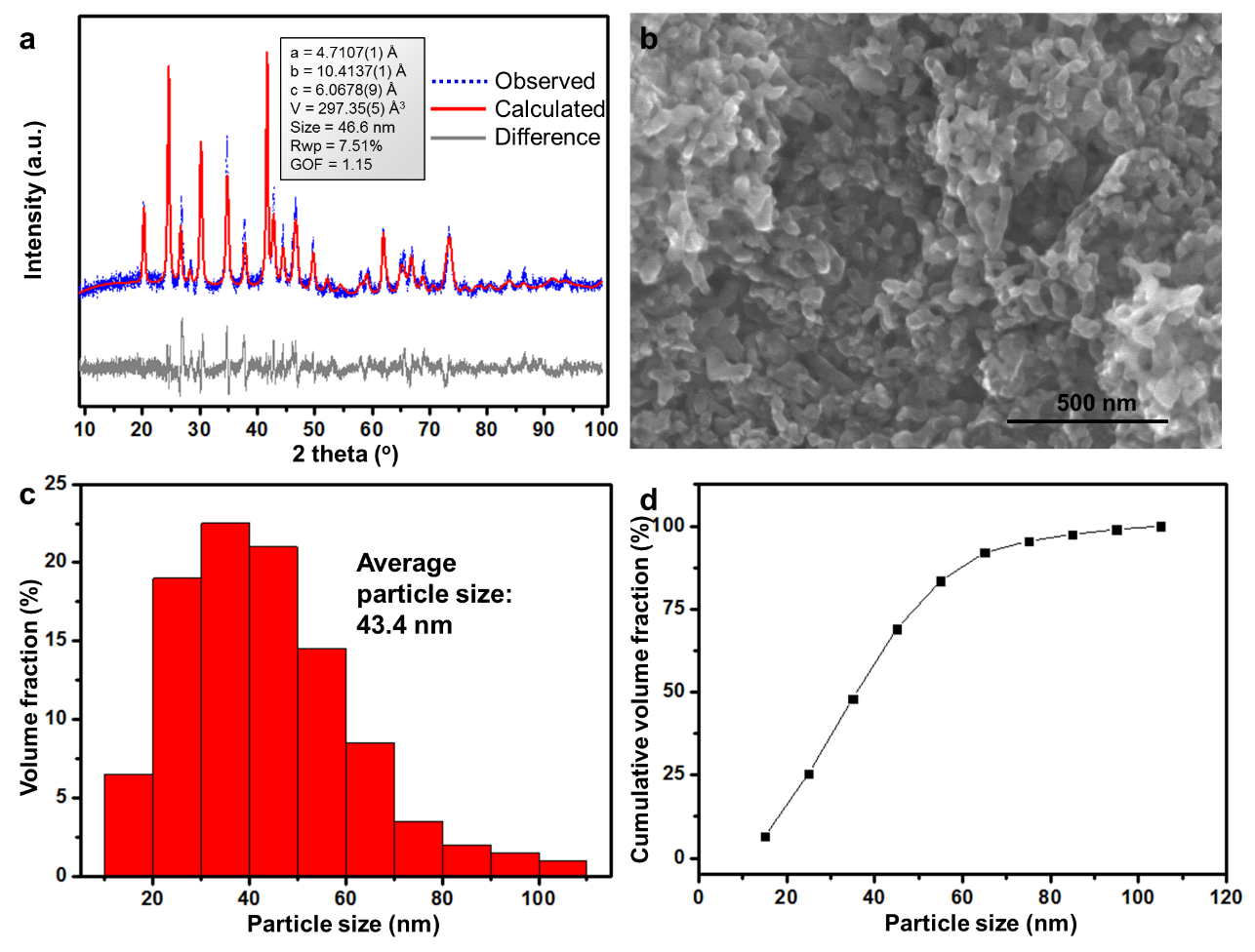
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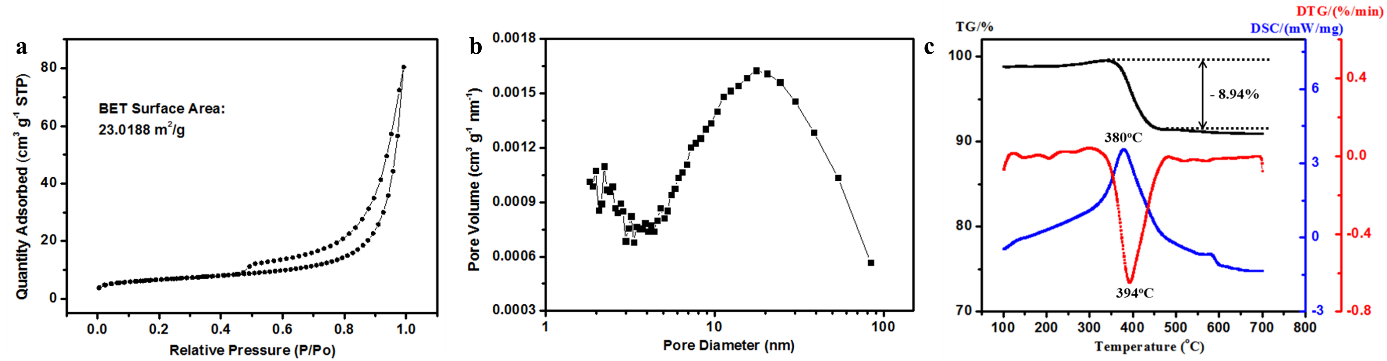
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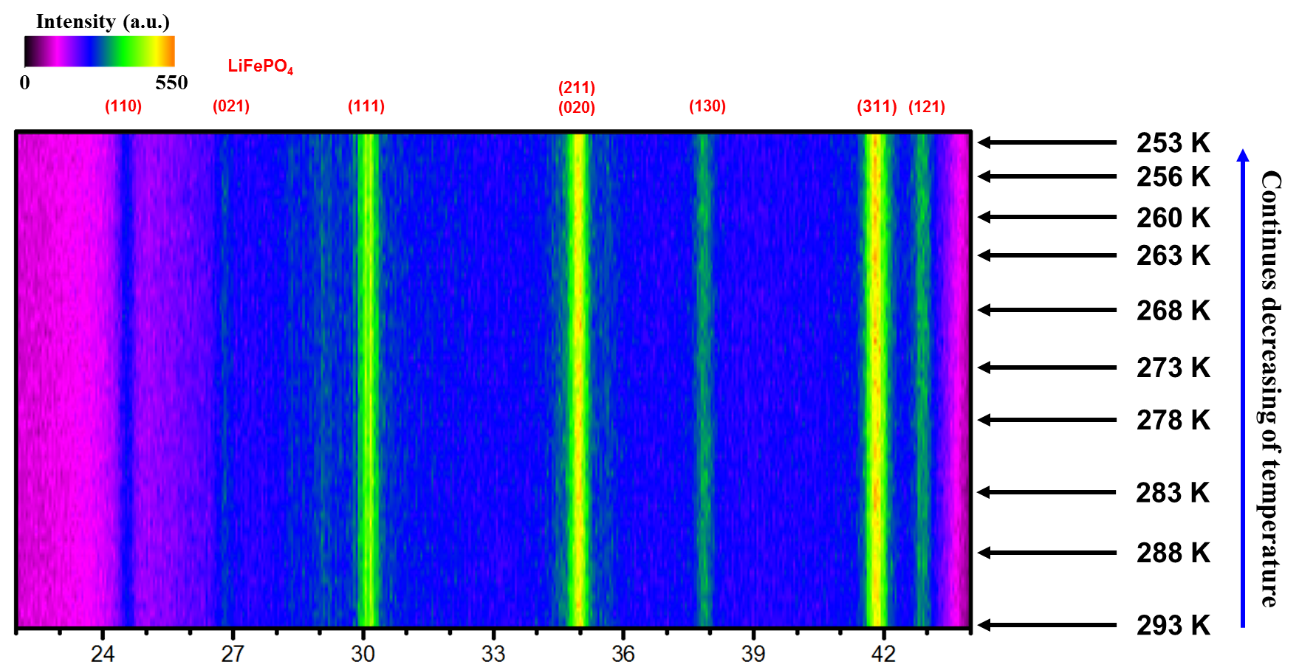
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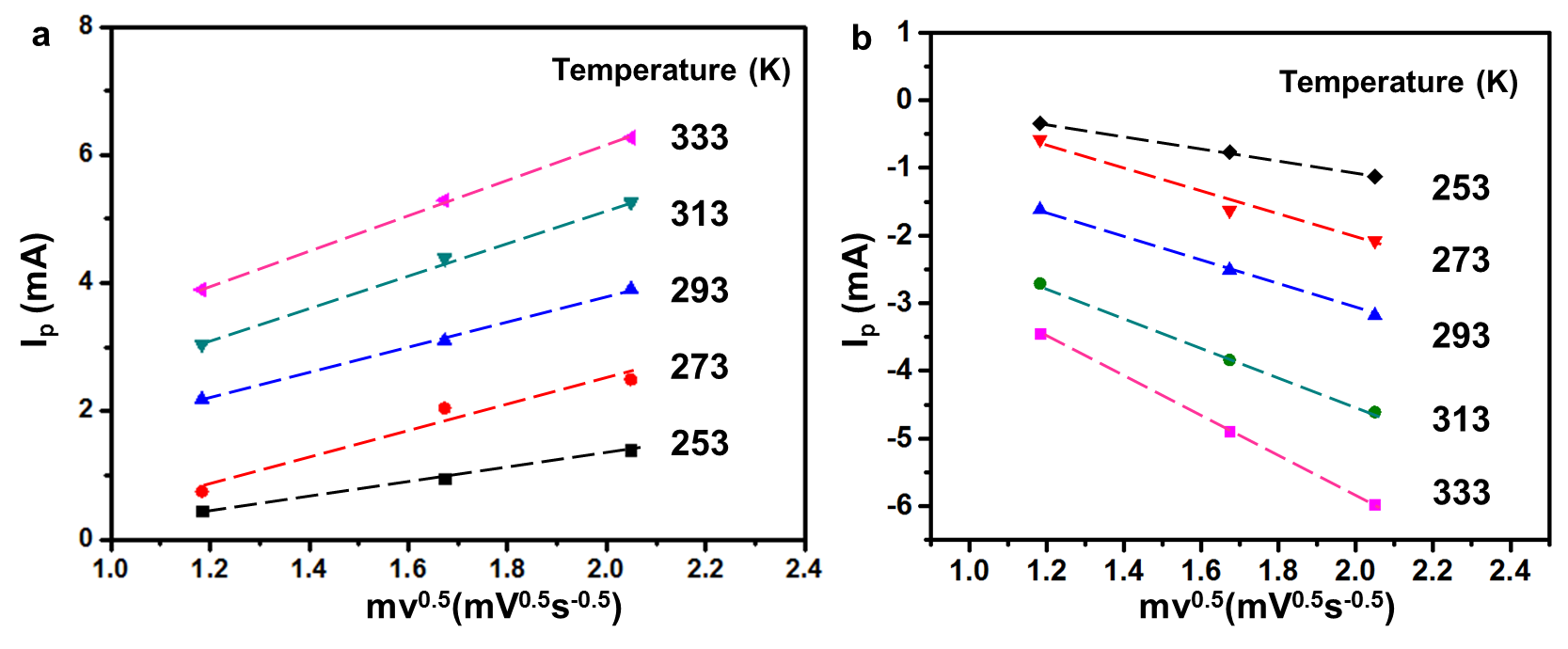
**Figure S1.** (**a)** Rietveld refinement of the X-ray diffraction data for the pristine LiFePO4/C. (**b )**The SEM image of LiFePO4/C. (**c, d)** the particle size distribution based on an analysis of 200 particles observed in the SEM images.



**Figure S2.** (**a**) nitrogen adsorption and desorption isotherms and (**b**) pore size distribution of the LiFePO4/C. (**c**) The TG (black line), DSC (blue line) and DTG (red line) curves of LiFePO4/C.

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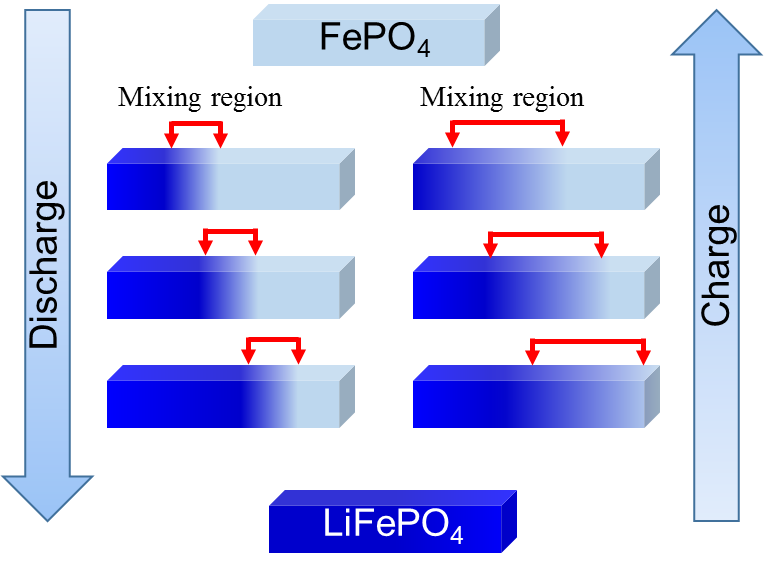
**Figure S3**. The XRD patterns of LiFePO4 at different temperatures.

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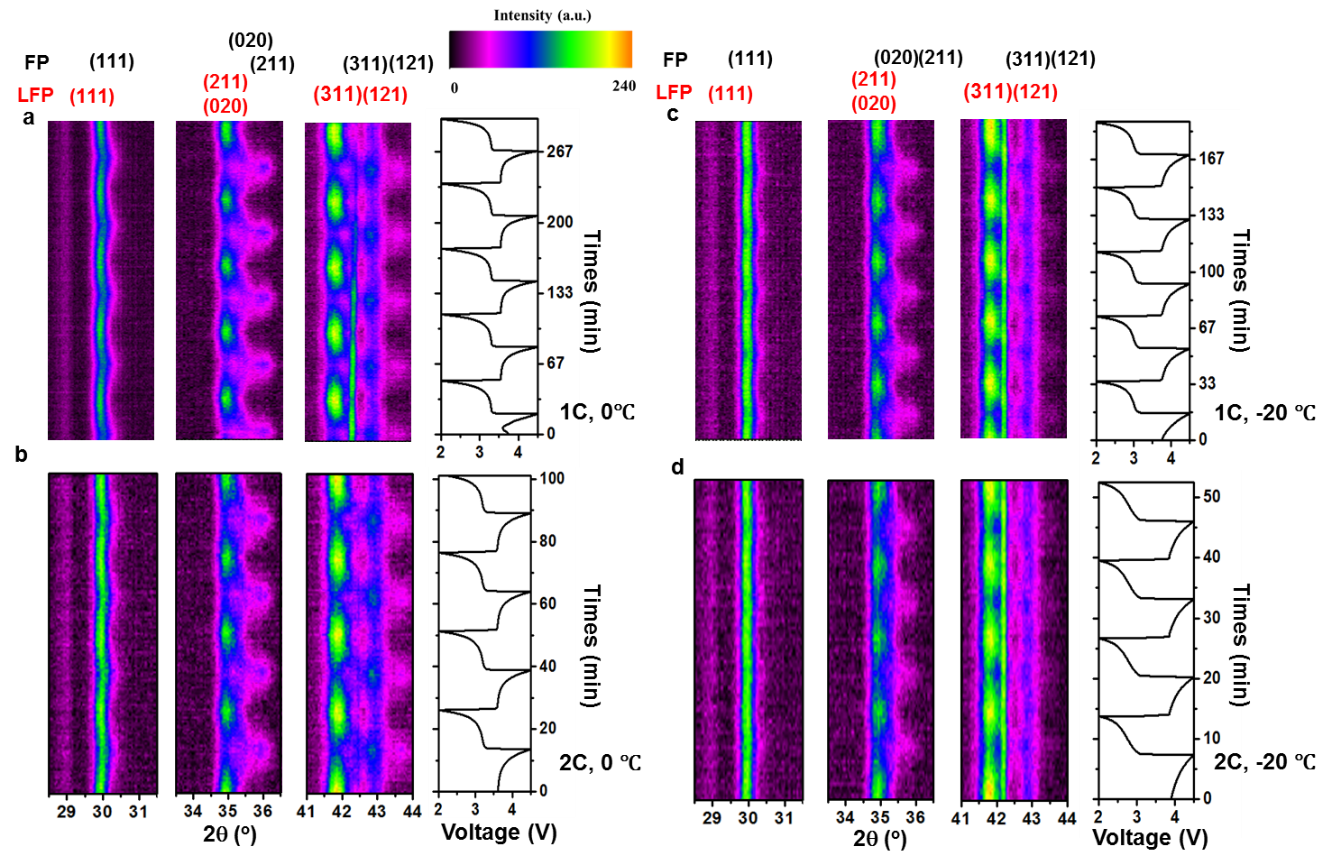
**Figure S4**. Linear fitting of Ip *vs* *v1/2* curves for the oxidation and reduction peaks in Figure 1a-c.

**Table S1**. Ion diffusion coefficients and corresponding degrade percentage per decreasing 20 K with different temperatures

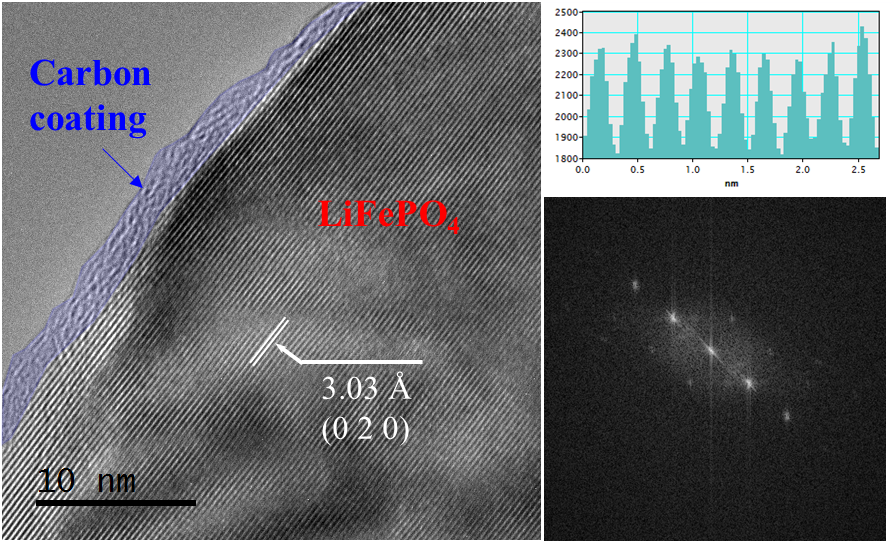
|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Temperature (K) | 333 | 313 | 293 | 273 | 253 | Average |
| Diffusion coefficients (cm2/s;  calculated from the oxidation peak) | 4.65E-13 | 3.84E-13 | 2.16E-13 | 2.14E-13 | 5.50E-14 | 2.67E-13 |
| Diffusion coefficient degrade percentage per decreasing 20 K (calculated from the oxidation peak) | — | 17% | 43% | 0.93% | 74% | 34% |
| Diffusion coefficients (cm2/s;  calculated from the reduction peak) | 4.32E-13 | 2.45E-13 | 1.65E-13 | 1.56E-13 | 4.21E-14 | 2.68E-13 |
| Diffusion coefficient degrade percentage per decreasing 20 K (calculated from the reduction peak) | — | 43% | 33% | 5.4% | 73% | 39% |



**Figure S5**. The schematic of the transformation of FePO4 and LiFePO4. The light blue, dark blue and the mixing region from light blue to dark blue represents the FePO4, LiFePO4 and solid solution between these phases, respectively.

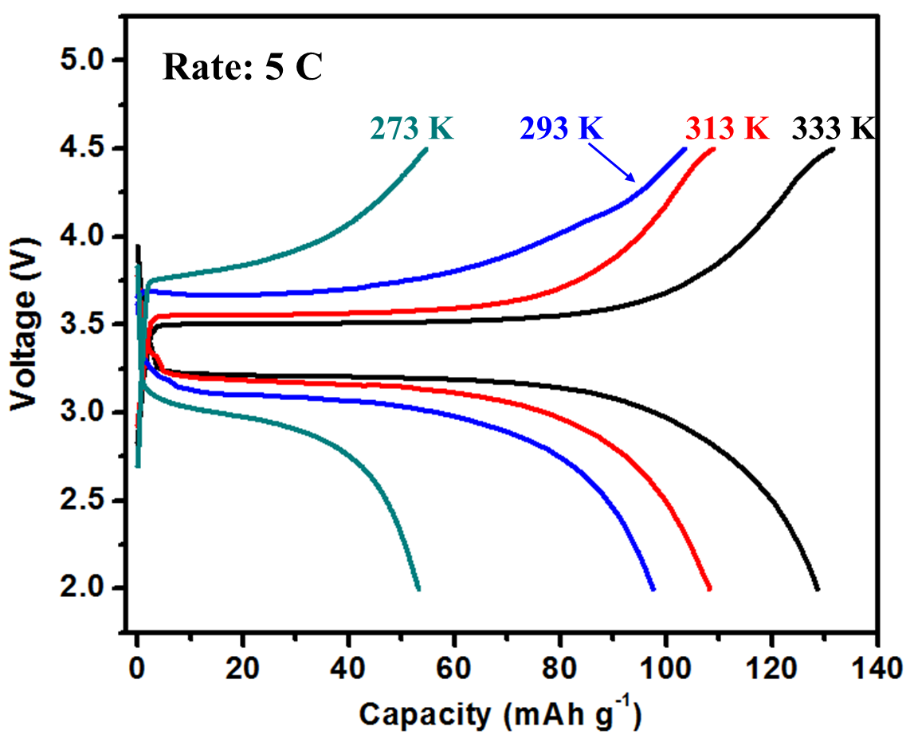


**Figure S6.** The image plot of diffraction patterns for (111), (211), (020), (311) and (121) reflections during the four charge/discharge cycles at a temperature of 273 K and 253 K with the scan rate of 1 C **(a, c)** and 2 C **(b, d).**

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**Figure S7.** The TEM image and corresponding Fast Fourier Transform image of LiFePO4.

The *ex situ* high resolution transmission electron microscopy (HRTEM) is applied to investigate the probable existence of intermediate phase of LiFePO4. (The electrode materials were taken out while the formation of intermediate phase and investigated by ex situ HRTEM) As shown in Figure S7, a lattice spacing of 0.303 nm is observed which matches well with the separation between (0 2 0) planes of LiFePO4. Although the intermediate phase is captured by high time resolution *in situ* XRD, there is no certain evidence which can demonstrate the existence of intermediate phase in *ex situ* HRTEM, which may be related to the really short life of such metastable state.



**Figure S8**. The charge-discharge curves of LiFePO4 with different reaction temperature of 273, 293, 313, 333 K at 5C.

The charge/discharge curves at different reaction temperatures (273, 293, 313, and 333 K) are shown in Figure S8. It is found that, the capacity of LiFePO4 can achieve a capacity of 131.4 mAh g-1 at 333 K with a rate of 5C. With the decrease of temperature to 313, 293 and 273 K, the capacity of LiFePO4 decrease to 108.8, 103.4, and 54.6 mAh g-1, respectively.

**Table S2**. Comparison of time resolution, testing temperature range, rate capability and cost with different X-ray sources and detectors.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **X-ray source** | **Time resolution** | **Testing temperature range** | **Rate capability** | **Cost** |
| Ordinary *in-situ* equipment (lab source) S1,S2 | 300 s | Room temperature | ~0.1 C | ~$ 200,000 |
| Our *in-situ* equipment (lab source, 2D detector) | 10 s | -20 - 60 oC | 5 C | ~$ 300,000 |
| Synchrotron X-ray source 27, S3 | 2.5 - 4 s | Room temperature | 20 C | Expensive |

There are two main advantages in this work. First of all, the lab X-ray source can achieve a high time resolution of 10 s, which is comparable to that of synchrotron X-ray source (3 – 4 s) and much higher than that of traditional in-situ equipment with lab source. This is benefitted from the application of two dimensional detector. Although the X-ray source intensity of lab technique is much lower than that of synchrotron technique, the signals of LiFePO4, FePO4 and corresponding intermediate phase is still obvious to the signals of noises. Secondly, the electrochemical reaction temperature is controllable (-20 – 60 oC). Thus, we are able to capture the metastable phase of LiFePO4 at different temperatures. Our discovery gives a deep understanding of the reaction dynamics of LiFePO4 at low temperature.

**References：**

[S1] X.-Q. Yang, J. McBreen, W.-S. Yoon, C. P. Grey, *Electrochem. Commun*. 4.8 (2002): 649-654.

[S2] Z. Lu, J. R. Dahn, *J. Electrochem. Soc.* 149.7 (2002): A815-A822.

[S3] H. Komatsu, H. Arai, Y. Koyama, K. Sato, T. Kato, R. Yoshida, H. Murayama, I. Takahashi, Y. Orikasa, K. Fukuda, *Adv. Energy Mater.* 5.17 (2015).