Electronic Supplementary Information for

Diffusion of Li-deficient phases in large LiFePO₄ single crystals during chemical delithiation

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1. Experimental setup



Figure S1

Figure S1 shows an illustration of the experimental setup for Raman spectroscopy. The system was explained in ref 21. Measurements were conducted in a dark space in a stainless box. An incident laser light was led by an optical fiber to the objective lens head and irradiated on the sample. Raman scattering signals were gathered by the same lens and guided to a spectrometer outside the stainless box by another optical fiber. The objective lens head was set on an x-y-z stage that was moved by stepping motors for scanning.



Figure S2

Figure S2 shows a photograph of the setup for Raman spectroscopy inside the stainless box.





Figure S3 shows an illustration of the setup for chemical delithiation of LiFePO₄. NO_2BF_4 /acetonitrile solution was put in a glass vessel. A separator film was wetted with the solution, and an LiFePO₄ single crystal was put on the separator film. A polypropylene lid with a hole that is larger than the crystal was used to minimize evaporation in order to avoid damage to the optics.



Figure S4

Figure S4 shows a photograph of the setup for chemical delithiation.



Figure S5

Figure S5 shows a photograph of the setup for chemical delithiation with a polypropylene lid.

2. Diffusivity and chemical potential

Generally, the flux, *J*, of diffusion of a component is proportional to the gradient of chemical potential, μ .²⁹⁻³¹ The force that particles of the component in the gradient of μ receive is as follows.

 $-d\mu/dz$ (per 1 mol)

 $-1/N \times d\mu/dz$, (per one particle of the component),

where N is the Avogadro constant and z is position. The final velocity is

 $-B/N \times d\mu/dz$,

where B is the mobility of particles. When each particle moves with this velocity, J is the number of particles in the volume determined as the product of unit area and velocity as follows:

$$J = -CB/N \times d\mu/dz, \qquad (1)$$

where C is the concentration of the component.

When C is low, the activity a of the component is proportional to C. In this case, μ is rewritten by equation (2).

$$\mu = \mu^0 + RT \ln a = \mu^{0'} + RT \ln C, \qquad (2)$$

where μ^0 is the standard chemical potential. Then the gradient of μ is described as follows:

$$d\mu/dz = 0 + RT/C \times dC/dz.$$
 (3)

By substituting formula (3) for (1), equation (4) is obtained.

$$J = -BRT/N \times dC/dz.$$
 (4)

If the diffusion coefficient, D, is defined as *BRT/N*, equation (4) becomes (5), which is often used as the definition of D (Fick's first law).

$$J = -DdC/dz.$$
 (5)