Supplementary information

Trackable galvanostatic history in phase separation based electrodes for lithium-ion batteries; mosaic sub-grouping intercalation model


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S Figure 1. Confirmation on pre-current effect with various galvanostatic current history.

a. Representative whole history of pre-current effect experiments. The pre-cycling is conducted with a current density of $x$ mA g$^{-1}$ ($x = 10, 30, 80, 130$ or $200$ mA g$^{-1}$) and the next following galvanostatic analysis is conducted with a current density $y$ mA g$^{-1}$ ($y = 10, 30, 80, 130$ or $200$ mA g$^{-1}$). The cut-off voltages are $2.5$ V (vs. Li/Li$^+$) for discharge and $4.6$ V (vs. Li/Li$^+$) for charge process, respectively. b. The first and second cycle over-lapped galvanostatic profiles as a function of SoC for $x = 10$ mA g$^{-1}$ and $30$ mA g$^{-1}$ case. c. $x = 30$ mA g$^{-1}$ and $10$ mA g$^{-1}$ case. d. $x = 30$ mA g$^{-1}$ and $80$ mA g$^{-1}$ case. e. $x = 80$ mA g$^{-1}$ and $30$ mA g$^{-1}$ case. f. $x = 130$ mA g$^{-1}$ and $200$ mA g$^{-1}$ case. g. $x = 200$ mA g$^{-1}$ and $130$ mA g$^{-1}$ case.
S Figure 2. Confirmation on the sequence dependency of pre-current effect.

a. The full history of electrochemical protocol. The applied current density is altered between 30 and 200 mA g\(^{-1}\) with three cycle intervals. 

b.-e. Zoomed-in charge profiles of the each interval. 

b. 4th, 5th and 6th charge profile with a current density of 200 mA g\(^{-1}\) after pre-cycling with 30 mA g\(^{-1}\). 

c. 7th, 8th
and 9th charge profile with a current density of 30 mA g\(^{-1}\) after pre-cycling with 200 mA g\(^{-1}\). d. 10th, 11st and 12nd charge profile with a current density of 200 mA g\(^{-1}\) after pre-cycling with 30 mA g\(^{-1}\). e. 13rd, 14th and 15th charge profile with a current density of 30 mA g\(^{-1}\) after pre-cycling with 200 mA g\(^{-1}\). The results clearly show that the current density of Nth cycle always affects on the galvanostatic profile of N+1th cycle, regardless of sequence.
Figure 3. Confirmation on the particle morphology after cycling. There is no significant degradation of the electrode materials such as particle cracking.

SEM images of the a – c. pristine electrode, d – f. 30 mA g⁻¹ and g – i. 200 mA g⁻¹ cycled electrodes. Note that the electrochemical cycle for cycled electrodes is performed with 10 times for each electrodes. In this experiment, cracking in the particles was not found in any part in electrode even after in the 200 mA g⁻¹ cycling. SEM results indicate that the change in the voltage profile is not due to the electrode degradation.
A comparison of the Nyquist plot on Li-Li symmetric cells after pre-cycling with current densities corresponding to 200 mA g\(^{-1}\) (black) and 30 mA g\(^{-1}\) (green) in Li-LFP cells. The cells were charged/discharged with a current density of 200 and 30 mA g\(^{-1}\) for 450 and 320 minutes, respectively, following three stabilization cycles. It is well known that the semi-circle in high frequency region is attributed to the impedance of lithium ion migration through the surface, which is interpreted as surface resistance induced by the solid electrolyte interphase (SEI) layer or changes in surface morphology. In this experiment, it is clearly showed that the surface resistance of lithium metal is slightly increased after the pre-cycling with a high current density (121.6 Ω) compared with the low current cycle (103.5 Ω). It indicates that the cell should exhibit higher polarization after a pre-cycling with high current density, which is exactly opposite to the pre-current effect, considering the behavior of the lithium metal electrode.
S Figure 5. Confirmation on pre-current effect with different pre-cycling current densities.

a. Whole history of electrochemical experiments. The pre-cycling is conducted with a current density of \( x \) mA g\(^{-1}\) (\( x = 80, 200 \) or 300 mA g\(^{-1}\)) and the next first galvanostatic profile is measured with a fixed current density of 80 mA g\(^{-1}\). b. The first cycles over-lapped galvanostatic profiles for pre-cycling with current densities of \( x = 80, 200 \) and 300 mA g\(^{-1}\).
S Figure 6. Confirmation on pre-current effect with different pre-cycling current densities.

a. Whole history of electrochemical experiments. The pre-cycling is conducted with a current density of $x \text{ mA g}^{-1}$ ($x = 30, 80, 200$ or $300 \text{ mA g}^{-1}$) and the next first galvanostatic profile is measured with a fixed current density of $30 \text{ mA g}^{-1}$. b. The first cycles over-lapped galvanostatic profiles for pre-cycling with current densities of $x = 30, 80, 200$ and $300 \text{ mA g}^{-1}$. 
S Figure 7. Confirmation on pre-current effect with different pre-cycling current densities.

a. Whole history of electrochemical experiments. The pre-cycling is conducted with a current density of $x$ mA g$^{-1}$ ($x = 10, 80, 200$ or $300$ mA g$^{-1}$) and the next first galvanostatic profile is measured with a fixed current density of 80 mA g$^{-1}$. b. The first cycles over-lapped galvanostatic profiles for pre-cycling with current densities of $x = 10, 80, 200$ and $300$ mA g$^{-1}$.

S Fig. 5-7 results show that the pre-current effect gets amplified as increasing differences between current densities of pre-cycle and first cycle even at various applied current densities.
S Figure 8. Pre-current effect on 1st discharge (for LFP) and 1st charge (for LTO).

(a-d). The whole galvanostatic history of LFP (a, b) and LTO (c, d) electrode. The right inset figures exhibit the over-lapped first, second and third discharge or charge profiles for each experiments. (a) and (c) experiment sets are operated with 200 mA g\(^{-1}\) cycling after 30 mA g\(^{-1}\) current histories. (b) and (d) experiment sets are conducted with 200 mA g\(^{-1}\) cycling after 30 mA g\(^{-1}\) current histories. Note that the S Fig 3 is a same experiment with a Fig 1 at main manuscript.
Cross sectional image of the LFP electrode. The electrode was uniformly casted on Al foil with a thickness ~ 40 μm. According to the previous reports on the electrode thickness effects on the electrochemical performances, the LFP electrodes under 50 micro meter thicknesses show no significant capacity reduction up to the current rates of ~10 C. It suggests that the electrochemical reaction inhomogeneity along the thickness direction might be negligible in our electrode that has been tested in much lower current density range (10 to 300 mA g⁻¹; 0.06 C to 2 C range) in our case.
S Figure 10. Particle morphology and particle size distribution of LiFePO$_4$ sample powder.

a,b. The SEM images of the prepared nano LFP powder in different magnifications.  
c. Particle size distribution of the prepared nano LFP.
**S Figure 11. Elemental analysis using energy dispersive spectrometer (EDS)**

**a.** SEM image of the location where the EDS was measured. EDS for **b.** carbon, **c.** iron, **d.** phosphorus and **e.** oxygen elements. **f.** Chemical composition report based on the EDS measurement results.
S Figure 12. Comparison on the fore one-phase reaction region of LFP electrode after pre-cycling with different current densities.

a. Experiments operated with 30 mA g\(^{-1}\) cycling after a 200 mA g\(^{-1}\) current history. b. Experiments operated with 200 mA g\(^{-1}\) cycling after a 30 mA g\(^{-1}\) current history. Note that the S Fig 5 (a) and (b) are same experiments with Figs 1 (a) and (b), respectively, at main manuscript. c. Experiments operated with 30 mA g\(^{-1}\) cycling after a 300 mA g\(^{-1}\) current history. d. Experiments operated with 300 mA g\(^{-1}\)
cycling after a 30 mA g\(^{-1}\) current history. e. Experiments operated with 130 mA g\(^{-1}\) cycling after a 200 mA g\(^{-1}\) current history. f. Experiments operated with 200 mA g\(^{-1}\) cycling after a 130 mA g\(^{-1}\) current history.
a

Pre-cycle
30 or 200 mA g\(^{-1}\)
First and second cycle
200 or 30 mA g\(^{-1}\)

Rest time
1 min, 1 hour or 3 hour

Time (hour)

b
c

d
e

First cycle
30 mA g\(^{-1}\)

2.0 mV
Pre-cycle: 200 mA g\(^{-1}\)
Rest time 1 min.

SoC (%)

200 mA g\(^{-1}\)

1.9 mV
Pre-cycle: 30 mA g\(^{-1}\)
Rest time 1 min.

SoC (%)

30 mA g\(^{-1}\)

1.2 mV
Pre-cycle: 200 mA g\(^{-1}\)
Rest time 1 hour.

SoC (%)

200 mA g\(^{-1}\)

1.4 mV
Pre-cycle: 30 mA g\(^{-1}\)
Rest time 1 hour.

SoC (%)

30 mA g\(^{-1}\)

0.1 mV
Pre-cycle: 200 mA g\(^{-1}\)
Rest time 3 hour.

SoC (%)

200 mA g\(^{-1}\)

0.8 mV
Pre-cycle: 30 mA g\(^{-1}\)
Rest time 3 hour.

SoC (%)
S Figure 13. Confirmation on rest time dependent pre-current effect between cycles.

a. Representative Galvanostatic history of experiments. The pre-cycling is conducted with a current density of 30 or 200 mA g\(^{-1}\) and the next following galvanostatic analysis is conducted with a current density 200 or 30 mA g\(^{-1}\). The rest time between all cycles is altered to 1 minute, 1 hour or 3 hours.  

b. Pre-cycling current density with a 200 mA g\(^{-1}\), rest time with 1 minute, and first and second cycle current density with a 30 mA g\(^{-1}\).  
c. Pre-cycling current density with a 30 mA g\(^{-1}\), rest time with 1 minute, and first and second cycle current density with a 200 mA g\(^{-1}\).  
d. Pre-cycling current density with a 200 mA g\(^{-1}\), rest time with 1 hour, and first and second cycle current density with a 30 mA g\(^{-1}\).  
e. Pre-cycling current density with a 30 mA g\(^{-1}\), rest time with 1 hour, and first and second cycle current density with a 200 mA g\(^{-1}\).  
f. Pre-cycling current density with a 200 mA g\(^{-1}\), rest time with 3 hours, and first and second cycle current density with a 30 mA g\(^{-1}\).  
g. Pre-cycling current density with a 30 mA g\(^{-1}\), rest time with 3 hours, and first and second cycle current density with a 200 mA g\(^{-1}\).

With increasing rest time, the over-potential differences between first and second cycle are obviously disappearing. For example, the gap at a 20 % SoC with an applied current density of 30 mA g\(^{-1}\) is 2.0 mV with 1 minute rest time (See Fig. S13 (b)), but the gap is reduced to 1.2 mV and 0.1 mV with rest time of 1 hour and 3 hours, respectively (See Fig. S13 (d) and (f)). These results not only prove that the lithium ion exchanges in solid-solution region require enough time to be fully united but also support that the sluggish kinetic property of Li\(_{1-x}\)FePO\(_4\) cause the memorization of thermodynamic driven mosaic instabilities.
S Figure 14. Confirmation on rest time dependent pre-current effect between half cycles.

a. Representative Galvanostatic history of experiments. The pre-cycling is conducted with a current density of 30 or 200 mA g$^{-1}$ and the next following galvanostatic analysis is conducted with a current density 200 or 30 mA g$^{-1}$. The rest time between half-cycle is altered to 1 minute, 1 hour or 3 hours. Note that the rest time between cycles is applied 1 minute. b. Pre-cycling current density with a 200 mA g$^{-1}$, rest time with 1 minute, and first and second cycle current density with a 30 mA g$^{-1}$. c. Pre-cycling current density with a 30 mA g$^{-1}$, rest time with 1 minute, and first and second cycle current density with a 200 mA g$^{-1}$. d. Pre-cycling current density with a 200 mA g$^{-1}$, rest time with 1 hour, and first and second cycle current density with a 30 mA g$^{-1}$. e. Pre-cycling current density with a 30 mA g$^{-1}$, rest time with 1 hour, and first and second cycle current density with a 200 mA g$^{-1}$. f. Pre-cycling current density with a 200 mA g$^{-1}$, rest time with 3 hours, and first and second cycle current density with a 30 mA g$^{-1}$. g. Pre-cycling current density with a 30 mA g$^{-1}$, rest time with 3 hours, and first and second cycle current density with a 200 mA g$^{-1}$.

The results of half-cycle rest are quite different from the results that the longer rest time between cycles alleviated pre-current effect (see Fig. S13), which well supports the proposed mosaic sub-grouping model. According to mosaic sub-grouping model, the chemical potential grouping of active particles occurs during application of the current density and the groups remain temporarily after the pre-cycle ends. Therefore, the pre-current effect in the first charge profile is only affect by rest time after discharge of pre-cycling (rest time between cycles) not by the rest time before discharge of pre-cycling (by the rest time between half cycles).
S Figure 15. Initial overshooting confirmation after pre-cycling with high current rate.

a. Whole history of galvanostatic cycling with a current density of 200 mA g\(^{-1}\) after 1000 mA g\(^{-1}\) pre-cycling. b. The first (red), second (black), third (blue) and fourth (wine) charge profile as a function of SoC.
Discussion 1. The more detailed discussion on the initial charging of non-uniform and uniform chemical distribution electrodes.

Here, it would be discussed on difference in the initial charging behaviors between non-uniform and uniform electrodes with respect to kinetic aspect of LFPs. Recently, Lim et al. experimentally demonstrated on the compositional variation of exchange current densities in LFP particles using the direct redox visualization tool\(^3\). The skewed \(J_0\) curve was obtained, and it should be noted that this shape of exchange current density had been already theoretically suggested by phase field modeling based on the solid-solution intercalation path of LFP\(^4\). Furthermore, they observed that the difference in lithium compositions between the nano-scale domains gradually increased during charging process, indicating that the certain domains participate in the electrochemical reaction more rapidly. It implies that the composition dependence of the rate constant (skewed \(J_0\) curve) amplifies this non-uniformity of electrochemical reaction during delithiation as follows; the domain starting with a higher exchange current density \((J_0)\) displays a higher electrochemical activity during the reaction owing to the Bulter-Volmer relation, and this domain would accept more currents than other slow domains starting with a lower exchange current density. Accordingly, the composition of the higher \(J_0\) domain would shift to delithiated composition firstly and again receive more positive feedback on the exchange current density, continuously leading to higher activity until the composition reaches \(x \approx 0.25\).

Now, let us apply this positive feedback scenario to the non-uniform electrode at the initial charging. The Fig. S16 shows the initial delithiation scenarios for the non-uniform electrode with respect to the chemical potential and the exchange current density. When the current is applied to the non-uniform electrode, each particle would accept different currents depending on their exchange current density of \(J_0\). Here, we denote the exchange current densities for particles 1’, 2’, 3’…, and \(n\) as \(J_{1'}, J_{2'}, J_{3'}...\), and \(J_{n'}\), respectively. (Note that each particle of 1’, 2’, 3’… are in slightly different SOCs in the initial state of the ‘non-uniform’ electrode.) At the initial state, the leading particles always have higher \(J_0\) than the following particles due to the slightly higher delithiated state \((J_1 > J_2 > J_3... > J_n\), Fig. S16 (a)). Accordingly, leading particles would accept more current corresponding to its higher electrochemical
activity, and the positive feedback occur more intensively for those leading particles (Fig. S16 (b)). This positive feedback on $J_0$ would keep the particle ‘order’ on the thermodynamic map during the initial charging as shown in Fig. S16 (a) to (b), and these processes would continue to the situation where only some of active particles are far ahead of others and induce the mosaic instability to reduce the overall free energy of the system (Fig. S16 (c)). The spinodal decompositions with a rapid delithiation occur on only limited number of active particles, which are far ahead of others due to the accelerated positive feedback and have enough driving force for phase separation (over the spinodal decomposition barrier, *i.e.* phase transition barrier, Fig. S16 (c) to (d)). At this time, the following particles (such as particles 5’, 6’…, and n’) below the barrier (which should be much smaller than a half of overall particles) are not going to actively participate in the phase separation because they have relatively lower driving force for the phase separation and exchange current density than the leading particles as shown in Fig. S16 (c).

If all the particle in the non-uniform electrode have to get over the phase transition barrier at a same time (Fig. S17 (a) to (b)), the following particles (such as particles 2’ and n’…) should take over more current than leading particles (such as particle 1’) to catch up leading particle’s chemical potential (Fig. S17 (b)). This scenario contradicts to the positive feedback (acceleration on delithiation) with the kinetic condition of $J_1 > J_2 > J_3 > \ldots > J_n$ at the initial state, thus it is hard to be established. From those thought experiments, we could conclude that the phase separation occurs with insufficient number of active particles in non-uniform electrode.

In the uniform electrode case, because there is no exchange current density difference among all the particles at the initial state ($J_1=J_2=J_3=\ldots =J_n$, Fig. S18 (a), down), the applied current will be ideally distributed with a ratio of 1/n to all the particles during the initial charging (Fig. S18 (a) to (b)). Thus, all the particle will follow the same chemical potential path and get over the phase transition barrier at the same time as shown in Fig. S18 (c). Consequently, relatively a large number of active particle would take part in the mosaic instability by spinodal decomposition compared with the non-uniform electrode case because all active particles have sufficient driving force for the phase separation (Fig. S18 (d)). It
should be noted that this kinetic scenario with phase transition barrier also well describes the observed lower overpotential of the uniform electrode than that of the non-uniform electrode because there is less current concentration to active particles in the uniform electrode.
S Figure 16. Initial charging scenario for non-uniform chemical potential distribution electrode with chemical potential (up) and exchange current density (down) maps.
S Figure 17. The scenario of chemical potential uniting for non-uniform electrode with chemical potential (up) and exchange current density (down) maps. This scenario means that the acceleration on delithiation rather happen in the following particles during the charging, which is in contrast to the kinetic condition of $J_1 > J_2 > J_3 > \ldots > J_n$ at the initial state, thus it is hard to be established.
Figure 18. Initial charging scenario for uniform chemical potential distribution electrode with chemical potential (up) and exchange current density (down) maps.
Discussion 2. The discussion on mosaic sub-grouping scenarios in actual battery system.

In order to illustrate the proposed model simply, we discussed mosaic sub-grouping scenarios without considering practical factors such as particle size distribution or uniformity of carbon coating in the main manuscript. However, it should be noted that the mosaic instability would be sensitively affected by the various factors such as the quality of LFP powders, thus, a more careful view on the mosaic sub-grouping scenario is necessary. For example, the relatively smaller active particles in the electrode would participate in the electrochemical reaction more actively than large particles, therefore, they would form the sub-groups first. Also, the chemical potential non-uniformity after the pre-cycling would disappear more rapidly with enhancing the carbon coating quality because the electrochemical interaction among active particles would be facilitated. Furthermore, since the top part of electrode is advantageous to participate the electrochemical reaction first due to the mass transport issues in electrolyte, it is highly likely to form mosaic grouping first. The proposed model represents an ideal case and, in actual situations, the grouping scenario would be altered by various kinetic factors.
References.


