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Influence of phase transformation pathways on electrochemical properties by using thermally derived solid-solution LiFePO_4 nanoparticles†

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To understand how a phase transformation pathway affects the electrochemical properties of LiFePO_4 nanoparticles (NPs), a sample with the solid-solution phase (SS sample) was prepared by thermal treatment of a sample that contained two phases, LiFePO_4 and FePO_4 , (TP). The SS sample had NPs that experience the solid-solution phase and then may undergo solid-solution phase transformation, and the TP sample had NPs that do not experience and then can undergo typical two-phase transformation. And their electrochemical characteristics were compared under various conditions. The thermodynamic properties of the two samples were evaluated using a galvanostatic intermittent titration technique (GITT) and a potentiostatic intermittent titration technique (PITT), and electrochemical kinetic properties were evaluated by applying current. The two samples had quite similar thermodynamic properties such as OCV and diffusion coefficient, but quite different kinetic properties such as polarization, current decay, voltage flatness and underpotential behavior even though they had a similar particle size and size distribution. The SS sample showed lower polarization, faster current decay at a constant voltage and less-significant underpotential behavior than did the TP sample. Furthermore, during charging/discharging, the voltage profile was a slope for the SS sample but flat for the TP sample even though the OCV of the two samples did not show any significant difference. These facile electrochemical characteristics can be related to nucleation indicating that the SS sample can have less significant nucleation than the TP sample. These different electrochemical properties are caused by different phase transformation pathways rather than the particle size that is the typical cause for those different kinetic properties. The phase transformation pathway of LiFePO_4 strongly affects the electrochemical kinetic properties, not the thermodynamic ones. We reveal that undergoing the solid-solution pathway can be kinetically better off leading to a fast electrochemical response.

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1. Introduction

LiFePO_4 (ref. 1) has superior thermal and structural stability with stable cycle life but insufficient power density because the properties of the material do not favor fast kinetics. For example, LiFePO_4 has poor electronic conductivity ($\sim 10^{-9}$ S cm^{-1} at room temperature RT)^{2,3} and one-dimensional lithium diffusion pathways that are easily blocked by transition metals.⁴ Furthermore, during charging or discharging, LiFePO_4 undergoes a phase-separation reaction that needs additional energy to form a secondary phase that induces large mechanical strain/stress due to its lattice mismatch.⁵ As a consequence, LiFePO_4 was believed to be a stable cathode material for low-

power rechargeable batteries. Although LiFePO_4 has insufficient properties to be a high power capable cathode, LiFePO_4 nanoparticles (NPs) show a very fast electrochemical response, and therefore have superior rate capability.^{2,6}

To understand the fast electrochemical response by LiFePO_4 NPs, a phase transformation pathway during charging/discharging should be considered because the particle size strongly affects the phase transformation reaction.⁷ In NPs, the formation of a secondary phase can require a large interfacial energy penalty at the interface between LiFePO_4 and FePO_4 because of their large surface area. Therefore, LiFePO_4 NPs can suppress the phase separation, thereby changing the phase separation mechanism. Single-phase particles are observed during charging/discharging; this observation indicates that phase separation in an NP can be suppressed.⁶ Furthermore, theoretical calculation suggests that an alternative phase transformation pathway such as a solid-solution reaction pathway can be stabilized.^{8,9} If LiFePO_4 NPs follow the solid-solution reaction pathway, their electrochemical activity can be

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kinetically advanced because the solid-solution reaction does not cause large mechanical stress and strain while extracting or inserting lithium. To verify the fast electrochemical response in LiFePO_4 NPs, many studies have focused on directly observing the solid-solution phase transformation pathway during charging or discharging in a cell.^{10–14} However, direct observation of the solid-solution phase during charging/discharging is not easy, because many factors affect the phase transformation behavior in a cell. Firstly, applying current or voltage in itself affects the phase transformation pathway.^{9,15} High current through an NP can suppress the phase separation behavior. A solid-solution-like phase has been observed at a very high rate of 20 C (3 min discharge) by using a specialized *in situ* set-up.¹⁶ Secondly, the flat voltage that originates from the non-monotonic chemical potential of Li can lead to inhomogeneous electrochemical reactions in the electrode, depending on the configuration of the electrode and the particle size distribution in the electrode.^{10,15,17,18} In this study, a different approach is used to gain understanding of phase transformation behavior in NPs. A sample with the solid-solution phase (SS sample) was prepared by thermal treatment of a sample that contained two phases, LiFePO_4 and FePO_4 , (TP sample). Then, the electrochemical properties of the two samples were evaluated under different electrochemical conditions. The SS sample has particles that start with the solid-solution phase and may undergo the solid-solution phase transformation during charging/discharging, but the TP sample has particles that start with the two end members and are not sure to undergo the solid-solution phase transformation. The thermodynamic and kinetic properties of the two samples were measured by a galvanostatic intermittent titration technique (GITT) and a potentiostatic intermittent titration technique (PITT) or by applying current. The electrochemical properties of the two samples were thermodynamically similar but kinetically quite different. The SS sample showed better kinetics even though the thermodynamic properties of the SS sample were similar to those of the TP sample. This finding indicates that following the solid-solution reaction pathway during charging or discharging can improve the kinetic properties of LiFePO_4 . The fast electrochemical response can be caused by the solid-solution reaction pathway. Different phase transformation pathways in LiFePO_4 strongly affect the kinetics of electrochemical properties rather than thermodynamic properties, and thereby lead to a fast electrochemical response.

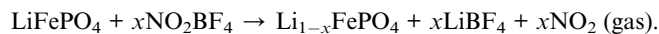
2. Experimental

2.1. Preparation of LiFePO_4

Nanosized LiFePO_4 samples were synthesized by a simple solid-state reaction. Stoichiometric amounts of lithium carbonate (Li_2CO_3 , JUNSEI >99%), iron(II) oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, Aldrich >99%) and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$, Aldrich >99%) were mixed by ball-milling. The mixture of precursors was dried and pelletized, and then subjected to two-step heat treatment (350 °C for 10 h and 600 °C for 10 h) under argon to obtain well-crystallized LiFePO_4 NPs.

2.2. Preparation of chemically delithiated Li_xFePO_4 and metastable solid-solution Li_xFePO_4

LiFePO_4 NPs were chemically delithiated to obtain two-phase $\text{Li}_{0.5}\text{FePO}_4$ (TP-LFP) by using nitronium tetrafluoroborate (NO_2BF_4 , Alfa Aesar >98%) in acetonitrile.¹⁹ The possible reaction is



The chemically delithiated sample was washed several times with acetonitrile and collected by centrifugation. The samples were dried on a hot plate at 80 °C in air. To prepare the SS Li_xFePO_4 sample, chemically delithiated samples with the two end members were annealed at 350 °C for 10 h, and then naturally cooled at RT.²⁰

2.3. Characterization of material properties

X-ray diffraction (XRD) patterns were obtained using a Rigaku MAX-2500 (Cu $K\alpha$). The morphology and particle size of samples were characterized using a scanning electron microscope (SEM) (Philips electron optics, XL30S).

2.4. Preparation of the electrode and electrochemical cell

LiFePO_4 , carbon (Timcal Super P carbon black), and polyethylenetetrafluoride, (PTFE, Dupont 8A) were mixed in a weight ratio of 45 : 50 : 5. A large amount of carbon in the electrode was used to ensure that electron transfer in the electrode was not limited. This cathode mixture was rolled into a thin sheet that had a uniform thickness and size. The electrode was incorporated into a Swagelok-type cell in a glovebox in which the H_2O level was controlled to be less than 1 ppm. The cell uses Li metal foil as the anode, a polypropylene film (Celgard 2400) as the separator, and 1 M LiPF_6 dissolved in a 1 : 1 mixture of EC and DMC as the electrolyte. The cells were galvanostatically charged and discharged over a range of applied voltage of 2.5 V–4.3 V at RT.

3. Results

3.1. Material characterization

The as-prepared TP sample had NPs with a particle size distribution (PSD) of 30–50 nm and a sphere-like morphology (Fig. 1a and c). The morphology and PSD (Fig. 1b and c) of the SS sample were similar to those of the TP sample. The delithiated amount of lithium, ~ 0.5 , was confirmed by Inductively Coupled Plasma (ICP) analysis. XRD patterns of the chemically delithiated SS sample and its TP samples are different from each other (Fig. 1d). The chemically delithiated sample clearly shows the two-end members, LiFePO_4 at 17° and FePO_4 at 18° (Fig. 1d). However, the XRD pattern of the SS sample shows several peaks, such as 17°–18°, $\sim 30^\circ$, 36°–37° and $\sim 40^\circ$, that are quite different from those of the TP sample. Rather, the XRD pattern of the SS sample is similar to that of LiFePO_4 without phase separation.²¹ Lattice parameters of the SS sample were $a = 10.083 \text{ \AA}$, $b = 5.905 \text{ \AA}$ and $c = 4.745 \text{ \AA}$; these are much smaller

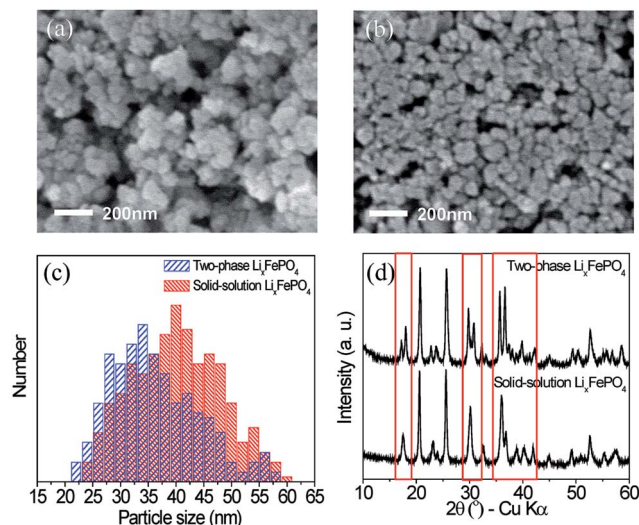


Fig. 1 SEM images of the (a) chemically delithiated two-phase $\text{Li}_x\text{-FePO}_4$ and (b) thermally derived solid-solution sample and (c) its corresponding particle size distribution. (d) XRD patterns of the two-phase sample and the solid-solution sample. $\text{Li}_x\text{-FePO}_4$ ($x \approx 0.5$). Red rectangular: angle ranges in which samples had different patterns.

than those of LiFePO_4 . The thermally derived SS sample did not go back to the two-end members even after 10 d relaxation at RT in the electrolyte.²²

3.2. Comparing the electrochemical properties of the SS sample and the TP sample under various electrochemical conditions

(i) Electrochemical properties under thermodynamic conditions. To evaluate the electrochemical properties of the two samples, the thermodynamic properties of the two samples were evaluated using a GITT, which has been widely used to evaluate the open circuit voltage (OCV), the diffusion coefficient, and the polarization. During GITT measurements, the cell was charged or discharged at a constant current of $C/50$ rate for an intermittent time of 1 h, followed by open-circuit relaxation for 3 h. The OCVs of the two samples were similar (Fig. 2a and c and Table 1). During charging, the OCV was slightly lower in the SS sample than in the TP sample; the magnitude of the difference reached 8 mV at the end of charging. During discharging, the OCV was slightly higher in the SS sample than in the TP sample; the difference was <5 mV; this similar OCV indicates that the thermodynamic properties do not differ much between the two samples even though one sample experienced the solid-

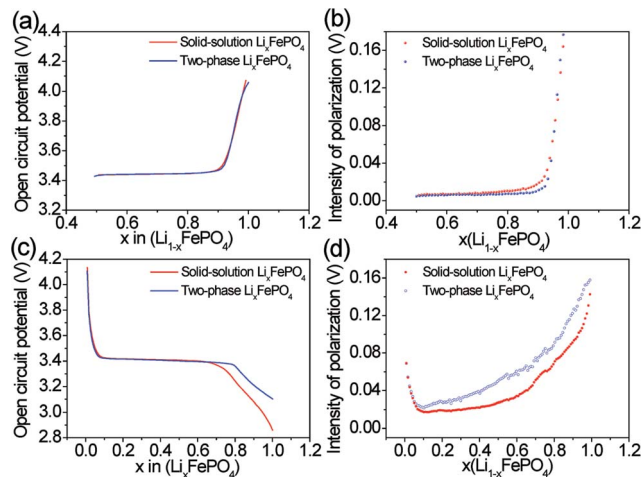


Fig. 2 GITT measurements of the solid-solution sample and the two-phase sample. (a) OCV and (b) polarization of the two samples during charge. (c) OCV and (d) polarization of the two samples during discharge.

solution phase transformation pathway and the other was not sure of the specific phase transformation mechanism.

Using GITT data, the diffusion coefficient of lithium ions can be calculated as²³

$$D_{\text{Li}^+} = \frac{4}{\pi} \left(\frac{V_M}{SF} \right)^2 \left(I_0 \frac{\delta E_s / \delta x}{\delta E / \delta t^{1/2}} \right)^2 \text{ at } t \ll \tau, \quad (1)$$

where V_M is the molar volume ($\text{m}^3 \text{mol}^{-1}$), S is the electrode surface area ($\text{m}^2 \text{g}^{-1}$), F is Faraday's constant (C mol^{-1}), I_0 is the current (A g^{-1}), $\delta E_s / \delta x$ is the slope of equilibrium open circuit potential versus lithium content (V s^{-1}), and $\delta E / \delta t^{1/2}$ is the slope of initial transient voltage charge versus square root of time t (s). Calculated $D_{\text{Li}^+} = 4.330 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$ for the SS sample and $2.427 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$ for the TP sample at 50% state of discharge; this difference is not large. The samples had similar OCV behaviors and diffusion coefficients to each other during both charging and discharging, and therefore had similar thermodynamic properties.

However, the SS sample showed much lower polarization than the TP sample in all composition ranges during discharging (Fig. 2d). The polarization in the SS sample was ~ 8 mV lower at the beginning and ~ 23 mV lower at the end than in the TP sample during discharging (Table 1). As a consequence, the SS sample could have better kinetics than did the TP sample. Typically, the polarization in the electrochemical cell has three origins: ohmic, concentration, and activation processes.²⁴ Ohmic polarization is related to the resistance of the cell and

Table 1 Voltage difference between the SS and TP samples at the state of charge and discharge $x = 0.2, 0.6$, and 0.9 in Fig. 2(a)–(d)

$V_{\text{SS}}/V_{\text{TP}}$ ($V_{\text{difference}}$)	$x = 0.2$	$x = 0.6$	$x = 0.9$
OCV in Fig. 2a		3.440/3.442 (2 mV)	3.470/3.462 (8 mV)
OCV in Fig. 2c	3.417/3.415 (2 mV)	3.401/3.397 (4 mV)	
Polarization in Fig. 2b		0.0065/0.0059 (0.6 mV)	0.0128/0.0097 (3.1 mV)
Polarization in Fig. 2d	0.019/0.027 (8 mV)	0.034/0.057 (23 mV)	

applied current; concentration polarization is related to the transport of salt in the electrolyte and applied current. Under GITT conditions (charge and discharge at $C/50$ rate), ohmic and concentration polarizations can be negligible. Therefore, the different polarizations in the two samples in GITT measurements can originate from activation (kinetic) polarization, which is related to phase transition reactions such as nucleation and charge transfer. Phase transformation can be easier in the SS sample than in the TP sample, so the former has much lower polarization than the latter even though two samples have similar thermodynamic properties. The two samples have a similar particle size, so the different electrochemical behaviors of the two samples are not due to the differences in the particle size distribution. Therefore, the different polarization behaviors in the two samples are probably due to the different phase transformation pathways.

To investigate the phase transition behavior of the two samples, the PITT was performed. For PITT measurements, 10 mV constant voltage was applied in a range of 2.5 V to 4.3 V and the response of current was measured. The single step of titration was continued until current decreased below the value of the $C/50$ rate. The two samples showed similar voltage profiles during charging and discharging (Fig. 3); this similarity is consistent with the results of the GITT (Fig. 2). However, during voltage hold, the current decayed quickly in the SS sample but slowly in the TP sample (Fig. 3). Decaying current can indicate the phase transition rate during the voltage hold. Phase transition was much faster in the SS sample than in the TP sample; as a result, the total time duration for charging/discharging was much shorter in the SS sample than in the TP sample. In particular, at the middle of charge, the decay of current was much slower in the TP than in the SS sample (Fig. 3a and b). Furthermore, at the beginning of the constant-voltage step, current was higher in the SS sample ($\sim 180 \mu\text{A}$) than in the TP sample ($\sim 80 \mu\text{A}$) (Fig. 3a and b). The current density can be related to the proportion of activated (lithiated/delithiated) particles.²⁵ Considering that the loading density of the electrode was lower in the SS sample than in the TP sample, the

high current in the SS sample indicates that a larger portion of particles can be activated at the same voltage step in the SS sample than in the TP sample. Moreover, the SS sample showed a monotonic current increase or decrease (Fig. 3a, arrow) whereas the TP sample showed a non-monotonic current increase or decrease (Fig. 3b). These results suggest that particles that experienced the solid-solution phase pathway can have better kinetic behaviors such as fast decay of current and large portion of activated particles, than did particles that did not sure to go through it.

(ii) **Electrochemical properties of the two samples under kinetic conditions (voltage profile under galvanostatic conditions, and rate capability).** The electrochemical properties of the SS sample and the TP sample were evaluated under galvanostatic conditions (Fig. 4). The initial charge capacities of the two samples were 70–80 mA h g^{-1} which match well with the amount of lithium ($x \sim 0.5$) in the sample. The two samples show quite different shapes of the voltage curve even though the OCV is similar to each other: the SS sample showed a sloped curve (Fig. 4b) whereas the TP sample showed a flat curve (Fig. 4a). However, differentiating phase transition behavior with respect to the flatness of the voltage curve requires careful examination.

To quantify the degree of flatness in the two samples, differential capacity plots were utilized (Fig. 4). Peaks in differential capacity plots were fitted with Gaussian functions to obtain Full Width at Half Maximum (FWHM) of the peaks. The SS sample had higher values of FWHM (0.031 for charge; 0.034 for discharge) than the TP sample (0.008 for charge; 0.010 for discharge). This difference indicates that the voltage profile of the SS sample is more sloping than that of the TP sample even though the two samples have similar particle sizes and size

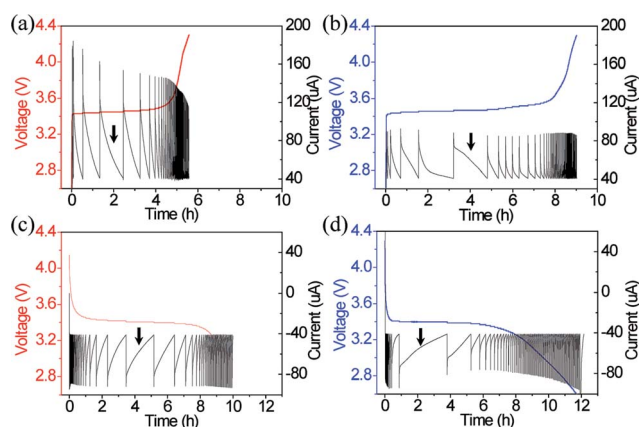


Fig. 3 Voltage steps and the corresponding current relaxation (black) during PITT measurements of the (a and c) solid-solution sample (6.36 mg cm^{-2}) and the (b and d) two-phase sample (6.96 mg cm^{-2}). Arrow: instance of non-monotonic change.

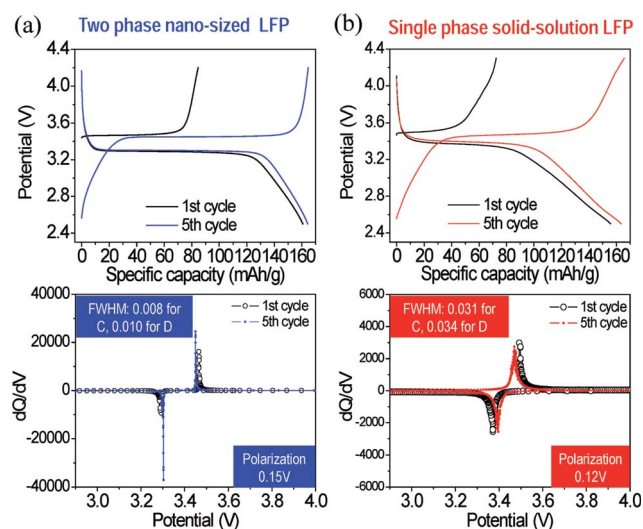


Fig. 4 Voltage profiles of the two samples in galvanostatic charge and discharge at $C/5$ rate and differential capacity plots for the two samples. (a) Two-phase sample (top) with its differential capacity plot (bottom) and (b) solid-solution sample (top) with its differential capacity plot (bottom). Loading density of the electrode was 4.87 mg cm^{-2} for the two-phase sample and 5.01 mg cm^{-2} for the solid-solution sample.

distributions. XRD patterns in Fig. S1† show that the SS sample was transformed to the LiFePO_4 or FePO_4 at the end of charge or discharge. Lattice parameters of the charged electrode were $a = 9.855 \text{ \AA}$, $b = 5.810 \text{ \AA}$ and $c = 4.782 \text{ \AA}$ and those of the discharged electrode were $a = 10.301 \text{ \AA}$, $b = 5.998 \text{ \AA}$ and $c = 4.695 \text{ \AA}$; these match well with those of bare LiFePO_4 and FePO_4 .^{21,22} Even though the SS sample was transformed to the two end members, the sloping voltage profile in the SS sample did not disappear even after several cycles (Fig. 4b). This observation indicates that different phase transformation pathways in the SS sample can affect the voltage profile. Furthermore, the voltage difference between charge and discharge was lower in the SS sample (0.12 V) than in the TP sample (0.15 V). The difference of the voltage may result from the low polarization of the SS sample because this sample shows both lower charging voltage and higher discharging voltage than the TP sample. This reduction of the polarization is consistent with GITT data. Considering that the two samples have similar particle size distributions, the sloping voltage behavior and the lower polarization during charging/discharging are not due to the particle size distribution²⁶ but can be due to the differences in phase transformation pathways. Particles that experienced the solid-solution reaction pathway showed a more sloped voltage curve and lower polarization under galvanostatic conditions than did the particles that did not.

The rate capabilities of the two samples were evaluated to determine their kinetic behaviors at a high rate. The electrode was charged at $C/5$ without holding at 4.2 V, and then discharged at 0.2 C, 1 C, 2 C or 20 C rates (Fig. 5). The loading density of the electrode was 3.98 mg cm^{-2} for the SS sample and 4.58 mg cm^{-2} for the TP sample. At a low rate, both samples showed almost a theoretical capacity of 165 mA h g^{-1} at 0.2 C rate, and as the current increased, the deliverable capacities of the samples were similar. However, at 20 C rate, the SS sample did not show any underpotential, whereas the TP sample showed a noticeable underpotential (Fig. 5b). The underpotential (or overpotential) can be related to nucleation in phase-separation compounds.²⁷ Therefore, the SS sample may not require the nucleation reaction in all particles at the beginning of discharge, but the underpotential in the TP sample indicates that the formation of LiFePO_4 may be required at the beginning of the discharge in this sample. The SS sample shows less significant nucleation than the TP sample on applying high current.

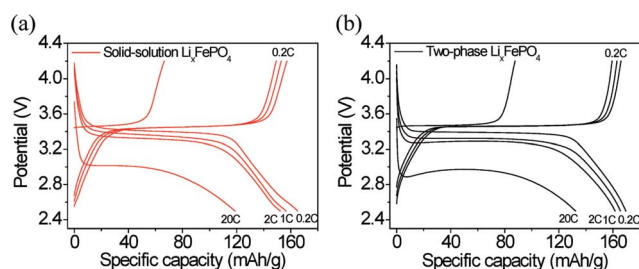


Fig. 5 Rate capabilities of the two samples (a) the solid-solution sample and (b) the two-phase sample.

4. Discussion

4.1. The two-phase sample and the solid-solution sample showed similar thermodynamic properties but different kinetic properties

Typically, the particle size strongly affects phase transformation behavior and therefore has a strong effect on electrochemical properties during charging/discharging.^{9,28} However, the effect of particle size on electrochemical properties can be ignored in this study because the two samples have similar particle sizes and size distributions. The SS sample and the TP samples represent particles that undergo different phase transformation pathways. Particles in the SS sample experienced the solid-solution pathway during charging/discharging whereas particles in the TP sample were not sure of the specific phase transformation pathway.

These characteristics of the two samples help us to understand how the phase transformation pathway affects electrochemical properties of LiFePO_4 NPs. The similarity in the thermodynamic electrochemical properties of the two samples indicates that different phase transformation pathways have little effect on the thermodynamic properties of the cell. In GITT and PITT data, the OCVs of the two samples were similar to each other over the entire range of lithium concentrations (Fig. 2 and 3). The two samples also had similar diffusivities, but had different electrochemical kinetic properties when current was applied. This difference indicates that different phase transformation pathways can affect the electrochemical kinetic properties of the cell. The SS sample can have better kinetic properties than the TP sample, leading to better electrochemical performance. For example, the SS sample achieves lower polarization in GITT data and faster decay of current in PITT data than the TP sample. Under GITT conditions, polarization can be from the activation process that is related to nucleation through the charge-transfer reaction on the surface. The lower polarization in the SS sample than in the TP sample indicates that nucleation can be easier in the former than in the latter. Furthermore, the current at the beginning in the constant voltage step in PITT data was much higher in the SS sample than in the TP sample even though the amount of active material was a little lower in the former than in the latter. Typically, the current at the beginning of delithiation can be related to the population of activated (delithiated) particles.²⁵ The high current in the SS sample indicates that a larger portion of particles can be activated in SS samples than in TP samples under the same voltage hold conditions. Considering that the two samples have a similar particle size, this larger portion of activated particles in the SS sample probably can be from less significant nucleation behavior. For instance, the SS sample can have much lower nucleation barrier than the TP sample leading to the activation of a large portion of particles. In the SS sample, nucleation may not occur or the nucleation barrier can substantially decrease in PITT data. Galvanostatic data such as rate capability and capacity retention further indicate that nucleation is much easier in the SS sample than in the TP sample. Under galvanostatic conditions, the SS sample showed

a sloping voltage profile with high FWHM (Fig. 4b) whereas the TP sample shows a flat voltage profile with low FWHM (Fig. 4a). Considering that the voltage flatness indirectly indicates whether LiFePO_4 undergoes first-order phase transition or others,²⁹ the observation of the sloping voltage curve in the SS sample during charging and discharging may indicate that the phase transition can progress by the solid-solution reaction pathway in a certain portion of the particles. Typically, the particle size distribution can induce a sloping voltage behavior.²⁶ However, these distributions are similar in the two samples, so the different voltage profiles of the two samples can result from the different phase transformation pathways rather than from the particle size distributions.

Furthermore, the TP sample showed high underpotential at a high discharge rate. Underpotential may be related to nucleation at the beginning of discharge; this indicates that nucleation to extract or insert lithium may be difficult in this sample, and that difficulty in nucleation can reduce the kinetics of the reaction. The PITT results are similar to these results. Current decay is related to lithium ion diffusion under external potential; this decay was clearly different in the two samples during lithiation (Fig. 3). At an applied constant voltage step of 10 mV, current decayed quickly in the SS sample but very slowly in the TP sample. Considering these differences of electrochemical properties between the two samples, the electrochemical kinetic properties are better in the SS sample than in the TP sample. This better kinetics in the SS sample may result from easier nucleation or less-significant phase-separation behavior compared to the TP sample.

In this study, we demonstrate that undergoing the solid-solution pathway in LiFePO_4 NPs can be kinetically beneficial. The finding indirectly confirms that the fast electrochemical response in LiFePO_4 NPs can result from undergoing the SS phase transformation pathway during charging/discharging. Undergoing the solid-solution reaction pathway in the SS sample can reduce the amount of nucleation during charging and discharging that can suppress phase separation behavior in particles and lead to fast kinetics. Furthermore, we demonstrate that the phase transformation pathway in LiFePO_4 NPs strongly affects their electrochemical kinetic properties but does not affect their thermodynamic properties. As a consequence, if the LiFePO_4 NPs can undergo the solid-solution phase transformation pathway by applying an external driving force such as high overpotential,^{18,25} the fast electrochemical response of LiFePO_4 can be achieved by different phase transformation pathways.

5. Conclusion

To understand how different phase transformation pathways affect the electrochemical properties of LiFePO_4 NPs, two samples in this study were prepared; one sample has NPs that experience the solid-solution reaction pathway and the other has the particles that are not guaranteed to undergo this pathway. The phase transformation pathway strongly affected the electrochemical kinetic properties of LiFePO_4 NPs, whereas it did not affect their thermodynamic properties. Quasi-OCV

curves from the GITT and PITT of the two samples were similar to each other, but the two samples showed quite different kinetic properties such as polarization and an underpotential behavior. The sample that underwent the SS phase transformation pathway showed lower polarization and less-significant underpotential behavior than did the TP sample. Furthermore, the SS sample showed a sloping voltage profile whereas the TP sample showed a flat voltage profile. These different electrochemical kinetic properties are caused by the differences in the phase transformation pathway, and not by the particle size and size distribution. Better electrochemical kinetic properties in the sample that underwent the solid-solution transformation pathway may result from facile nucleation or less significant nucleation. Based on the finding, we can reveal that the fast electrochemical response in LiFePO_4 NPs can be ascribed to different phase transformation pathways such as the solid-solution one.

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References

- 1 A. K. Padhi, K. S. Nanjundaswamy and J. B. Goodenough, *J. Electrochem. Soc.*, 1997, **144**, 1188.
- 2 S. Y. Chung, J. T. Bloking and Y. M. Chiang, *Nat. Mater.*, 2002, **1**, 123.
- 3 P. S. Herle, B. Ellis, N. Coombs and L. F. Nazar, *Nat. Mater.*, 2004, **3**, 147.
- 4 P. Gibot, M. Casas-Cabanas, L. Laffont, S. Levasseur, P. Carlach, S. Hamelet, J. M. Tarascon and C. Masquelier, *Nat. Mater.*, 2008, **7**, 741.
- 5 G. Y. Chen, X. Y. Song and T. J. Richardson, *Electrochem. Solid-State Lett.*, 2006, **9**, A295.
- 6 B. Kang and G. Ceder, *Nature*, 2009, **458**, 190.
- 7 C. Delmas, M. Maccario, L. Croguennec, F. Le Cras and F. Weill, *Nat. Mater.*, 2008, **7**, 665.
- 8 R. Malik, F. Zhou and G. Ceder, *Nat. Mater.*, 2011, **10**, 587.
- 9 P. Bai, D. A. Cogswell and M. Z. Bazant, *Nano Lett.*, 2011, **11**, 4890.
- 10 G. Ouvrard, M. Zerrouki, P. Soudan, B. Lestriez, C. Masquelier, M. Morcrette, S. Hamelet, S. Belin, A. M. Flank and F. Baudet, *J. Power Sources*, 2013, **229**, 16.
- 11 M. Bianchini, J. B. Leriche, J. L. Laborier, L. Gendrin, E. Suard, L. Croguennec and C. Masquelier, *J. Electrochem. Soc.*, 2013, **160**, A2176.
- 12 D. Robert, T. Douillard, A. Boulineau, G. Brunetti, P. Nowakowski, D. Venet, P. Bayle-Guillemaud and C. Cayron, *ACS Nano*, 2013, **7**, 10887.
- 13 J. J. Wang, Y. C. K. Chen-Wiegart and J. Wang, *Nat. Commun.*, 2014, **5**, 4570.
- 14 J. J. Wang and X. L. Sun, *Energy Environ. Sci.*, 2015, **8**, 1110.

- 15 Y. H. Kao, M. Tang, N. Meethong, J. M. Bai, W. C. Carter and Y. M. Chiang, *Chem. Mater.*, 2010, **22**, 5845.
- 16 H. Liu, F. C. Strobridge, O. J. Borkiewicz, K. M. Wiaderek, K. W. Chapman, P. J. Chupas and C. P. Grey, *Science*, 2014, **344**, 1480.
- 17 G. Oyama, Y. Yamada, R. Natsui, S. Nishimura and A. Yamada, *J. Phys. Chem. C*, 2012, **116**, 7306.
- 18 M. Tang, W. C. Carter, J. F. Belak and Y. M. Chiang, *Electrochim. Acta*, 2010, **56**, 969.
- 19 A. Wizansky, P. Rauch and F. Disalvo, *J. Solid State Chem.*, 1989, **81**, 203.
- 20 H. J. Tan, J. L. Dodd and B. Fultz, *J. Phys. Chem. C*, 2009, **113**, 20527.
- 21 C. Delacourt, P. Poizot, J. M. Tarascon and C. Masquelier, *Nat. Mater.*, 2005, **4**, 254.
- 22 S. Yoo and B. Kang, *Nanotechnology*, 2013, **24**, 424012.
- 23 W. Weppner and R. A. Huggins, *J. Electrochem. Soc.*, 1977, **124**, 1569.
- 24 K. B. Oldham, J. C. Myland and A. M. Bond, *Electrochemical Science and Technology: Fundamentals and Applications*, 2012, ch. 10.
- 25 Y. Y. Li, F. El Gabaly, T. R. Ferguson, R. B. Smith, N. C. Bartelt, J. D. Sugar, K. R. Fenton, D. A. Cogswell, A. L. D. Kilcoyne, T. Tyliczszak, M. Z. Bazant and W. C. Chueh, *Nat. Mater.*, 2014, **13**, 1149.
- 26 A. Van der Ven and M. Wagemaker, *Electrochem. Commun.*, 2009, **11**, 881.
- 27 B. Kang and G. Ceder, *J. Electrochem. Soc.*, 2010, **157**, A808.
- 28 D. A. Cogswell and M. Z. Bazant, *Nano Lett.*, 2013, **13**, 3036.
- 29 R. Malik, A. Abdellahi and G. Ceder, *J. Electrochem. Soc.*, 2013, **160**, A3179.