Columnar order in jammed LiFePO4 cathodes: ion transport catastrophe and its mitigation

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Columnar order in jammed LiFePO$_4$ cathodes: ion transport catastrophe and its mitigation

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The high-rate, high-capacity potential of LiFePO$_4$-based lithium-ion battery cathodes has motivated numerous experimental and theoretical studies aiming to realize such performance through nano-sizing, tailoring of particle shape through synthesis conditions, and doping. Here, a granular mechanics study of microstructures formed by dense jammed packings of experimentally and theoretically inspired LiFePO$_4$ particle shapes is presented. A strong dependence of the resultant packing structures on particle shapes is observed, in which columnar structures aligned with the [010] direction inhibit diffusion along [010] in anisotropic LiFePO$_4$. Transport limitations are induced by [010] columnar order and lead to catastrophic performance degradation in anisotropic LiFePO$_4$ electrodes. Further, judicious mixing of nanoplatelets with additive nanoparticles can frustrate columnar ordering and thereby enhance the rate capability of LiFePO$_4$ electrodes by nearly an order of magnitude.

Introduction

Olivine lithium metal phosphates, such as LiFePO$_4$, are an emerging class of cathode materials for the development of low-cost, environmentally benign lithium ion batteries (LIBs).$^1$ Recent broad-based scientific research plans, such as the Materials Genome Initiative,$^2$ have recognized that the rapid translation of energy storage materials to the commercial market requires the utilization of physics-based multi-scale modeling to inform experimental efforts. In this spirit we investigate ion transport in dense cathodes of LiFePO$_4$ and find that rate performance depends strongly on adverse granular-scale columnar order. The mechanisms leading to catastrophic ion transport rate reduction are elucidated, and mitigation strategies are identified to achieve the full rate capability of LiFePO$_4$.

The anisotropic olivine structure and chemical interactions result in unique properties that emerge in nanoscopic forms of LiFePO$_4$. In general, reduction of particle size has generally improved electrochemical performance.$^{3–5}$ Insertion of lithium in bulk FePO$_4$ occurs via a two-phase process wherein lithium ions diffuse from a lithium-deficient phase into a lithium-rich phase,$^6$ which can change to a single-phase process in nanoscale systems.$^7,8$ Ion diffusion is one-dimensional in anisotropic nanoscale LiFePO$_4$,$^9–13$ and experimental evidence suggests that (de)intercalation can occur via propagation of a two-phase interface perpendicular to the highly diffusing direction.$^{14–16}$ These findings have been supported by theoretical analysis of ‘intercalation waves’,$^{17}$ but recent analyses have revealed that such a mechanism is suppressed by dynamic$^{18,19}$ and mechanical effects.$^{20}$ Despite these nanoscale effects, long-range ionic and electronic transport through electrolyte, binder, and additive carbon wiring networks limits capacity in thick composite electrodes.$^{21–24}$ Consequently, thin electrodes are desirable for high rate applications because fast nanoscale mechanisms (e.g., solid-state ion diffusion) limit discharge therein.

The theories of morphological effects on transport in composite LiFePO$_4$ cathodes lack experimental pathways to achieving such microstructures. For instance, mesoscopic particle clustering,$^{25}$ graded porosity,$^{26}$ particle size,$^{25}$ inter-penetrating electrodes,$^{26}$ continuous phase distribution,$^{27}$ fractal phase distribution,$^{28}$ and distribution of particle size and conductive additives$^{29}$ have been considered. These theories also fail to incorporate the variety of particle shapes and diffusion anisotropy exhibited by LiFePO$_4$. Experimental attempts have been made to maximize [010] surface area of particles normal to the highly diffusing [010] direction in LiFePO$_4$.$^{30,31}$ Additionally, recent experimental observations of shape through transmission electron microscopy$^{32}$ and through X-Ray diffraction broadening analysis$^7$ enable more precise representations of realistic particle shapes. $Ab$ initio models of LiFePO$_4$ crystal growth have predicted particle shapes under both thermodynamic equilibrium$^{32–33}$ and non-equilibrium$^{32}$ conditions.

Granular materials exhibit a liquid-solid transition referred to as the jamming point, and at this point such media can...
support infinitesimal stress without yielding. Recent studies have revealed that jammed systems of superellipsoids, superballs, and cubes can exhibit liquid crystalline phases with particles having negligible kinetic energy. Self-assembly of mesoscopic particles (e.g., colloids and nanoparticles) has been pursued as a route to fabricate a variety of composite materials. In particular, rules governing self-assembly have been suggested to tune interactions among anisotropic particles to avoid amorphous or glassy structures. Self-assembly and amorphous particulate structures predicted by simulations (e.g., gravitational sedimentation, mechanical contraction method, thermodynamic Monte Carlo, and athermal jamming) can vary unless such structures are in the same mechanical state undergoing similar local interactions. The jamming point is such a generic unifying state at which to compare structures, as it has proven consistency of structure between hard and soft particle systems. Such packing effects are critical for LiFePO$_4$-based cathodes. Despite possessing 10% higher gravimetric capacity than LiCoO$_2$, which is the current industry standard cathode material, LiFePO$_4$ possesses 20% lower volumetric capacity.

In the present work we investigate the structures of high-density, many-particle assemblies of experimentally and theoretically inspired LiFePO$_4$ nano-crystal shapes via granular jamming and assess the galvanostatic discharge performance of the resulting heterogeneous media. These structural effects cause a predictable (and preventable) ion transport catastrophe in anisotropic LiFePO$_4$.

**Jamming of LiFePO$_4$ particles**

A variety of theoretically (A1, A2, A3, B) and experimentally (C1, C2, C3, D, sphere) inspired particle shapes relevant to LiFePO$_4$ are studied in this work (Fig. 1). Geometric parameters describing each shape are listed in the Appendix. Shapes A1 and B are equilibrium crystal shapes determined by Wulff construction with surface energies simulated in ref. 32 and 33, respectively. The construction of shape A1 is consistent with that of ref. 33, while shape B differs slightly from that in ref. 32 (see Appendix). To simulate the effect of changing the chemical state of the (010) surface, surface energy was varied from the value used to obtain A1, as suggested in ref. 33, to obtain shapes A2 and A3. Shapes C1, C2, and C3 represent homologous variations of the shape presented in ref. 32 based on transmission electron microscopy images. Shape D was inspired by the shape of ref. 7 estimated via spherical harmonic analysis of X-ray diffraction broadening. Spherical nanoparticles have also been synthesized experimentally.

We explore the structural effects occurring when ensembles of these shapes are densely jammed together from an initially dilute, random state (Fig. 2). Details of the jamming simulation are described in the Models and Methods section. Of particular interest is the phenomenon of columnar ordering in which particles tend to form stacks with many face–face contacts between orientationally-ordered particles as the systems are jammed into high density structures (Fig. 2). To link shape to the structure of jammed systems quantitatively we define the aspect ratio of each shape as $\alpha = \sqrt{A_{\text{max}}/A_{\text{min}}}$, where $A_{\text{max}}$ and $A_{\text{min}}$ are the maximal projected surface area among all possible directions and the thickness of the shape normal to the projection direction of $A_{\text{max}}$, respectively. Hereafter we refer to isometric shapes as nanoparticles; these shapes are A1, B, and the sphere, exhibiting aspect ratios of 0.80, 0.97, and 0.79, respectively. Shapes A2, A3, C1, C2, and C3 are nanoplatelets with the largest face normal to the [010] direction and exhibiting aspect ratios of 1.5, 5.2, 5.2, 10, and 21, respectively. Shape D exhibits an aspect ratio of 2.9 and is also a nanoplatelet but with the [010] direction in the plane of the largest face.

The morphological similarities among these shapes suggest that similar jammed structures will be formed, but the crystallographic orientation of nanoplatelets may either have a benign or catastrophic effect on ion transport. For example, nanoparticle (A1, B) jam into disordered structures with 93% and 98% of surface area normal to [010] exposed to electrolyte, respectively. The lack of columnar ordering in these systems is evidenced by column heights limited to $2t_{[010]}$, and is illustrated for shape B nanoparticles in Fig. 3(a). Columnar ordering in the system of shape D is beneficial to lithium ion transport because (010) faces are arranged on the periphery of self-assembled columns exposed to electrolyte [Fig. 3(b)]. Consequently, 98% of surface area normal to the [010] direction is preserved upon jamming of the system with shape D, suggesting that ion transport performance will be relatively uninhibited by dense packing.

The remaining nanoplatelets (A2, A3, C1, C2, C3) display largest faces normal to [010], and columns therein obscure (010) faces from electrolyte [Fig. 3(c)]. In general, as the aspect ratio $\alpha$ of nanoplatelets increases, columnar order increases, as reflected by increasing average column height $h$ and decreasing (010) surface area exposed to electrolyte [Fig. 3(d)]. Most notably, the largest aspect ratio nanoplatelet system (C3) has only 31% of its (010) surface area exposed to electrolyte, which should be measurable experimentally via gas adsorption. The mean column height of this system is quite large ($\bar{h} \approx 6t_{[010]}$) implying that one-dimensional channels are substantially longer on average than those of isolated nanoplatelets. Our observations of structure in jammed systems are consistent with those of...
Fig. 2 Microstructural development of a system of C2 nanoplatelets during jamming. Density φ, listed below each snapshot, indicates the progression from a dilute, random system to a dense, jammed system. Periodic boundaries of the cube-shaped primary simulation cell are indicated by black edges. Color indicates the height of columns to which nanoplatelets belong in the jammed structure at φ = 0.768.

Fig. 3 Jammed structures of (a) 100 B nanoparticles, (b) 100 D nanoplatelets, and (c) 400 C2 nanoplatelets. Color indicates the height of columns to which particles belong. (d) Exposed (010) surface area relative to isolated particles (white symbols) and average column height (gray symbols) as a function of nanoplatelet aspect ratio. Triangular symbols are for systems of 400 C2 nanoplatelets and 200 C3 nanoplatelets, while the remaining points are for systems of 100 particles. Periodic boundaries of the cube-shaped primary simulation cell are indicated by black edges.

Saravanan et al., Chen and Dahn, and Dokko et al., each of whom reported inhibition of electrolyte penetration and subsequent reduction of electrochemical performance due to the agglomeration of nanoplatelets [Fig. 8(b)]. Importantly, we distinguish that columns are more than simple disordered agglomerates—they are self-assembled structures with local orientational order in each column. These structures form in jammed systems that lack thermal agitation, despite assertions in the literature that jamming and other phenomena relevant to particulate systems “threaten” ordering.

Columnar order causes obscuration of the most chemically active surfaces (e.g., for systems of shapes A2, A3, C1, C2, and C3) and requires mitigation for optimal battery performance (i.e., rate and capacity). Here a granular mixing mitigation strategy, schematically depicted in Fig. 4, is considered whereby LiFePO4 nanoplatelets of certain aspect ratio and size are mixed randomly with nominally spherical additive nanoparticles of diameter d; the primary function of additive nanoparticles is to introduce steric defects between pure nanoplatelets to frustrate columnar ordering. The effectiveness of this approach is evident from our initial studies on mixtures of 66 vol % LiFePO4 mixed with additive nanoparticles having a size of d = 1.5t[010] in which column heights are drastically reduced by the presence of additive [cf. Fig. 4 left and middle]. This frustration is also reflected by a reduction in the average column height from 2.4t[010] in the pure system to 1.1t[010] in the mixed system. The introduction of electrochemically inactive additive (e.g., non-activated carbon) decreases the gravimetric capacity of cathodes, with the most extreme case being no LiFePO4 present in the system (Fig. 4, right). Therefore an optimal amount of frustrating material should be added to achieve high rate performance and high capacity.

**Topological structure analysis**

The distribution of one-dimensional diffusion channel lengths is analyzed by considering the geometric topology of such channels in jammed structures (e.g., columns). This detailed analysis reveals the contrasting structural mechanisms that inhibit ion transfer in columnar ordered and disordered systems. For systems whose columnar axes are aligned with [010], opposing faces in a given column prevent electrolyte access and increase the channel length, L, through which ions diffuse [Fig. 5(a)]. Considering individual columns [Fig. 5(a)] it is apparent that they do not form with perfect alignment in the direction transverse to the column axis. Consequently, a distribution of channel lengths at integer multiples of t[010] exists [Fig. 5(b)]. Enhanced columnar order with increased aspect ratio results in the emergence long channels. This characteristic is particularly apparent for the largest aspect ratio system (C3), where channels of length t[010] up to 7t[010] exhibit nearly equal volume in the jammed microstructure. Short channel lengths result from the random transverse alignment of nanoplatelets on the periphery of columns [Fig. 5(a) light tan], while longer channels reside in the interior of the column [Fig. 5(a) dark blue]. Comparison of the channel length distributions of pure and mixed systems of C1 nanoplatelets in Fig. 5(b) quantitatively confirms that columnar order frustration reduces diffusion length scales in jammed microstructures as the volume of minimal length channels increases from 45% in the pure system to 79% in the mixed system.
Columnar order is not present in jammed systems of shapes A1 and B, and though present in the system of shape D it does not increase diffusion channel lengths. Only mild obscuration of (010) faces occurs in these systems, and the mechanism of obscuration is very different than in the [010] columnar systems.

Fig. 4  Facile mitigation of columnar order via mixing of LiFePO₄ nanoplatelets with additive nanoparticles. The key parameters in such mixtures include nanoplatelet concentration, the thickness and aspect ratio of nanoplatelets \( t_{[010]} \) and \( a \), respectively, and the volume effective diameter of nanoparticles \( d \). Columnar order exhibited by the pure nanoplatelet system (left) is frustrated as additive nanoparticles are added to the mixture (middle). The mixed system (middle) contains 100 C1 nanoplatelets (66% by solid volume) and 640 additive icosahedra with \( d = 1.5t_{[010]} \). At low LiFePO₄ concentration (right) the system is composed primarily of electrochemically inactive additive particles. Color indicates the height of columns to which LiFePO₄ particles belong. Periodic boundaries of the cube-shaped primary simulation cell are indicated by black edges.

Fig. 5  (a) Cross section of a column from a system of C3 nanoplatelets. Channels are colored according to the length along the highly diffusing direction. (b) Volume distribution of channel lengths for systems of nanoplatelets having largest face normal to [010]; C1 mix is a binary system of 66 volume % C1 nanoplatelets with additive icosahedra having a volume effective diameter of 1.5\( t_{[010]} \). (c) Examples of capped channels formed in systems of shapes B, D, and A1. Arrows indicate highly diffusing directions. (d) Continuous and discrete contributions to the volume distribution of channel lengths in systems in which the dominant mechanism of electrolyte access restriction is by channel capping.

Columnar order is not present in jammed systems of shapes A1 and B, and though present in the system of shape D it does not increase diffusion channel lengths. Only mild obscuration of (010) faces occurs in these systems, and the mechanism of obscuration is very different than in the [010] columnar systems.

Most face–face contacts involving a single (010) face occur with a low-diffusion (100) or (001) face of the opposing particle, as shown in Fig. 5(c). Consequently, ions are incapable of traversing the interface between particles. Such contacts, therefore, induce a capping effect on channels of the particle...
contacting with its (010) face. The path through which ions must flow effectively doubles the channel diffusion length relative to the unjammed systems [Fig. 5(d)]. The capping effect most significantly affects shape A1, while the small surface area of the (010) faces of shape B and the columnar ordering of shape D reduce the number of (010) face contacts and consequently capping of those faces [Fig. 5(d)].

Systems of spheres, shape B, and shape A1 exhibit a continuous distribution of channel lengths [Fig. 5(d)] that occurs because the lengths of channels exposed to electrolyte on faces other than the (010) planes vary with position on these surfaces. Conversely, for shapes having only (010) faces that are diffusively active (A2, C1, C2, C3, D) only discrete distributions of channel length exist. Spheres possess many channels with lengths below \( t_{010} \), followed by systems of shape B, and subsequently shapes of shape A1. We find that in all systems the contribution by very short channels (\( L < t_{010} \)) to the total channel volume was negligibly changed as a result of jamming.

**Discharge dynamics**

Each aforementioned system is subjected to simulated galvanostatic discharge \((i.e., \text{liithiation of FePO}_4)\) at constant current per unit volume, \( I \), until a threshold cell potential of 2 Volts is reached. The solid-state ion transport model assumes that face–face contacting particles form polycrystals in which electrolyte cannot penetrate face–face contacting interfaces \((i.e., \text{electrolytic wiring between face–face contacting particles is very poor})\). We consider discharge rates of \( I = nC \), where \( C \) corresponds to a rate of 170 mA/g-LiFePO\(_4\), and determine the resulting discharge capacity of the cathode by simulating diffusion in one-dimensional channels of jammed LiFePO\(_4\) particles. The intrinsically fast diffusion of lithium along \([010]\) is impeded by lithium-iron anti-site defects.\(^{11}\) Also, the trapping efficacy of anti-site defects increases with particle size.\(^{11}\) Consequently, two-dimensional diffusion has been observed in macroscopic LiFePO\(_4\) with 2.5\% anti-site defects.\(^{10}\) In the present work the trapping efficacy of such anti-site defects in nanoscale LiFePO\(_4\) is neglected and therefore one-dimensional diffusion along [010] is considered.\(^{20}\) Also, well-wired, thin cathodes are considered here in which long-range transport limitations resulting from electronic conduction and salt diffusion are negligible. Electrolyte potential is therefore considered uniform throughout the cathode. Li diffusion and electrolyte-LiFePO\(_4\) surface reaction are the competing particle-scale mechanisms leading to capacity reduction. For the high discharge rates of interest in this work, intercalation will occur in the diffusion-limited regime,\(^{51}\) though many recent studies have focused on the surface reaction limited regime.\(^{17,19,20}\) Additionally, LiFePO\(_4\) may undergo a two-phase or single-phase intercalation mode depending on the size of nanoparticles and the rate of discharge.\(^{11,18–20}\) Therefore, the discharge dynamics of the present systems under study are considered separately for both modes: two-phase and single-phase intercalation. For both modes inter-channel diffusion and intercalation wave mechanisms are neglected, and concentration independent diffusivity is considered. The dependence of two-phase interface orientation on electrochemical conditions and particle size is not fully resolved,\(^{52}\) and therefore a simplified model for such is employed here. In the two-phase mode separation is modeled \(\text{via a shrinking core}^{34}\) where the lithium-rich/deficient phase interface in each channel is represented as a discontinuity in the concentration field; this model contrasts with the diffuse interface representations in phase field\(^{17,55}\) and mushy zone\(^{56}\) models. Further details of the models employed here are described in the Models and Methods section.

The ensemble of [010] channels and the distribution of length scales displayed in Fig. 3(b) and (d) result in unique discharge dynamics for both intercalation modes. Channels of the same length \( L \) in a given system are intercalated at the LiFePO\(_4\)-electrolyte interface with ion surface flux \( j_{IS} \) (in units of mol/m\(^2\)-s). Integration of ion surface flux over the LiFePO\(_4\)-electrolyte interface yields total discharge current (in units of mA). The galvanostatic discharge condition \(i.e., \text{I = constant})\) and spatially uniform electrolyte potential couple discharge among the distribution of channels. The capacity of each system has been simulated for a range of galvanostatic discharge rates with common thickness \( t_{010} = 20 \text{ nm}, \text{diffusivity, and discharge kinetics.} \)

**General features**

The system of C3 nanoplatelets, which exhibits the strongest columnar ordering among all nanoplatelets investigated, illustrates important features of the transient variation of ion

![Fig. 6](image-url)
surface flux (Fig. 6) for each channel in the system. The rates of discharge for the systems represented in Fig. 6 correspond to those concomitant with a capacity of 120 mA-hr/g. The two-phase discharge process [Fig. 6(a)] proceeds via diffusion through the lithium-rich shell that induces conversion from a lithium-deficient phase at the interface between the two phases. At the initiation of discharge, all channels exhibit the same ion surface flux, because interface motion is unimpeded. After approximately 1700 s the interface in the smallest channel \( L = 2 \ell_{010} \) reaches its terminal position, and single-phase conversion ensues in that channel. Coincidentally, ion surface flux decreases in that channel as a result of increased surface concentration and the concomitant decrease in equilibrium surface potential. Ion flux on the remaining channel surfaces \( L > 2 \ell_{010} \) increases accordingly to maintain galvanostatic conditions. Eventually, two-phase conversion terminates in the next largest channel, \( L = 2 \ell_{010} \), inducing increased ion surface flux in longer channels. Initially the single-phase discharge process [Fig. 6(b)] proceeds in a manner similar to the two-phase process, because the ion diffusion front propagates in a manner similar to the two-phase interface. In contrast, when an ion diffusion front reaches its terminal position in a given channel its utilization is much lower than the utilization of the same channel undergoing two-phase diffusion. Consequently, short channels continue to intercalate substantially after the front has terminated. For both modes of diffusion this sequence of interface/front propagation and termination proceeds successively throughout the distribution of channel lengths (whether discrete or continuous) until discharge terminates.

**Rate performance: common particle size**

The maps of capacity versus dimensionless discharge rate, \( n \), contain a region in which systems undergo ion transport catastrophe due to strong columnar order along [010] [Fig. 7(a) and (b), gray masks]; these maps also contain a region lacking structure-anisotropy correlation for which jamming has little influence on ion transport irrespective of two-phase [Fig. 7(a)] or single-phase [Fig. 7(b)] diffusion. The capacity at which termination occurs is affected primarily by high discharge rates in large channels leading to large concentration gradients and consequently high Li concentration at the solid surface. Because of the decreasing equilibrium cell potential of LiFePO\(_4\) with Li concentration, this high concentration terminates the discharge process with low capacity utilization in channels not converted fully to lithium-rich phase. In columnar microstructures this behavior causes tremendous loss relative to the ideal capacity, because large channels undergo only partial intercalation. As a result systems of nanoplatelets with strong columnar ordering along [010] (C3, C2, A3, C1) exhibit dramatically lower capacity at a given rate than the other systems (sphere, B, D, A1, A2, C1 mixture). The effect is very significant, as C3 nanoplatelets undergoing two-phase intercalation must be discharged at a rate 30 times less than the high-rate systems to yield a capacity of 120 mA-hr/g. In general, rate performance decreases with the extent of columnar ordering along [010]. For two-phase intercalation, discharge capacity varies with dimensionless discharge rate more smoothly for spheres and systems of shape B than for other shapes because of the more even distribution of channel lengths in the former systems. Also, the nanoplatelet system of shape D exhibits very similar rate capability at a capacity of 120 mA-hr/g to spheres and the jammed system of shape B. The efficacy of our columnar order mitigation strategy is also evidenced by the results. The C1-additive mixture exhibits 6.6 and 3.3 times enhancement in rate capability relative to the pure system of C1 nanoplatelets at 120 mA-hr/g for two-phase and single-phase intercalation, respectively. Specifically, the low volume fraction of columns with length \( L > 2 \ell_{010} \) results in high utilization of LiFePO\(_4\).

The effect of columnar order on rate performance is substantial for both two-phase and single-phase intercalation processes but is more significant for two-phase intercalation. The root cause of the severity of rate performance reduction during two-phase intercalation is revealed in the discharge dynamics of C3 nanoplatelets [Fig. 6(a)]; in that system only channels up to length \( 2 \ell_{010} \) have terminated interface propagation, and the maximal length channel has \( L = 9 \ell_{010} \). In contrast, the same system exhibits enhanced flux from long channels when undergoing single-phase conversion [Fig. 6(b)].

**Rate performance: experimental particle size limits**

Even though spherical nanoparticles offer the best performance among all the shapes investigated when \( \ell_{010} \) is fixed, experimental evidence indicates that the minimum possible \( \ell_{010} \) depends on particle shape. In particular, the smallest particles have been synthesized as nanoplatelets [e.g., < 20 nm in ref. 31], while only larger isometric particles [e.g., 50 nm in ref. 4] have been synthesized. However, we are also cognizant of the rapid advances in nanofabrication and the likelihood that these limits will change in the future. Direct comparison of the experimental data to the present theoretical result is difficult because of the variety of synthesis conditions employed (e.g., low temperature precipitation,\(^7\) solid-state,\(^4\) and solvothermal\(^3\) syntheses). Synthesis conditions are known to influence the concentration of lithium anti-site defects and crystallinity that will affect ion diffusion.\(^11,57\) as well as miscibility gap.\(^7,8\) Therefore, we have simulated the rate performance of several experimentally realized particle shapes at a capacity of 120 mA-hr/g, as displayed in Table 1, with the same diffusivity. Spheres and systems of shape D prevail in performance among pure systems, as a result of columnar order in systems of shapes C3 and C1, but in contrast to the results for equally sized particles (Fig. 7), the mixed system among these more practical cases exhibits substantial enhancement relative to others irrespective of the intercalation mode.

**Rate-independent capacity reduction**

In the previously presented diffusion analysis perfect continuity of solid LiFePO\(_4\) at interfaces between particles is assumed, such that diffusion across interfaces is unimpeded. In such cases, reduced capacity is a result of concentration gradients developed at high discharge rates. In contrast, if organic moieties are trapped between particle surfaces at an interface or if substantial roughness is present, transfer of lithium ions across such interfaces may be inhibited. Such behavior was observed in the work of Saravanan et al.,\(^31\) as low capacity was observed even at very low discharge rates. When such interfaces...
are impenetrable to lithium ions, the electrochemically active mass in which intercalation may occur is reduced by inactive interior regions of columns [Fig. 8(a), dark blue]. Only LiFePO₄ mass accessible without crossing a solid–solid interface [Fig. 8(a), light yellow] is therefore an active intercalation host. Columnar aggregates similar to those in jammed nanoplatelet systems have been observed experimentally [Fig. 8(b)]. Because this capacity reduction mechanism is rate-independent it must receive technological consideration even in low-rate battery applications.

Fig. 7 Discharge capacity as a function of dimensionless discharge rate for systems undergoing (a) two-phase and (b) single-phase diffusion. The curve for each system is marked by a thumbnail of its jammed microstructure, where each particle is colored according to the column height in terms of the minimum thickness \( t_{min} \) of each LiFePO₄ shape. The region of strong [010] columnar order is marked by gray masks. Horizontal lines indicate the 120 mA-hr/g performance threshold.
Table 1: Dimensionless discharge rate at which 120 mA-hr/g galvanostatic discharge capacity is achieved, \( n_{120 \text{mA-hr/g}} \). Thickness \( t_{010} \) listed for each shape is the minimal value achieved in the cited references. Discharge rate listed for the sphere is for a single particle, whereas the remaining values are those of jammed systems. C1 mix is a mixture of 66 vol % C1 nanoplatelets with additive icosahedra having a volume effective diameter of \( d = 1.5 t_{010} \).

<table>
<thead>
<tr>
<th>Shape</th>
<th>( t_{010} ) (nm)</th>
<th>( n_{120 \text{mA-hr/g}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>sphere</td>
<td>50 [Ref. 4]</td>
<td>5.8 35</td>
</tr>
<tr>
<td>D</td>
<td>40 [Ref. 7]</td>
<td>6.6 32</td>
</tr>
<tr>
<td>C3</td>
<td>20 [Ref. 31]</td>
<td>0.81 5.6</td>
</tr>
<tr>
<td>C2</td>
<td>20 [Ref. 31]</td>
<td>1.8 13</td>
</tr>
<tr>
<td>C1</td>
<td>20 [Ref. 31]</td>
<td>3.3 24</td>
</tr>
<tr>
<td>C1 mix</td>
<td>20 [Ref. 31]</td>
<td>22 79</td>
</tr>
</tbody>
</table>

Fig. 8 (a) Half of a single column within a jammed system of C3 nanoplatelets. Portions of the column are accessible to lithium ions without traversing an interface as indicated in light yellow, while in the remaining interior portion, indicated as dark blue, ion transfer may be inhibited depending on any interfacial barriers (e.g., surface roughness or organic moieties). (b) Similar columnar agglomerates have been observed experimentally by Saravanan et al. Reproduced by permission of the Royal Society of Chemistry.

The active mass of jammed LiFePO\(_4\) systems is presented in Table 2, based on channel length distributions in Fig. 5(b) and (d). Channels of length \( t_{010} \) and \( 2t_{010} \) are fully active, while only the peripheral volume in larger channels are accessible. Consequently, the active volume fraction in each such channel \( i \) will be \( 2t_{010}/L_i \). Active material content decreases with increasing columnar order along [010], with the C3 system having only half its LiFePO\(_4\) mass accessible to lithium ions. The enhancement of active material obtained with the introduction of additive species is also clear: the C1 mix case is nearly fully active, while its pure counterpart exhibits approximately 10% inactive material. The remaining systems contain channels with at most one face–face interface in each channel, and therefore achieve full utilization. This capacity reduction mechanism reveals that connections between granular structure and ion transport are strong irrespective of electrode thickness and the quality of long-range wiring.

Table 2: Active percentage of LiFePO\(_4\) in jammed systems with impenetrable solid–solid interfaces. C1 mix is a mixture of 66 vol % C1 nanoplatelets with additive icosahedra having a volume effective diameter of \( d = 1.5 t_{010} \).

<table>
<thead>
<tr>
<th>Jammed system</th>
<th>Active %</th>
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<tbody>
<tr>
<td>C3</td>
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</tr>
<tr>
<td>C2</td>
<td>79.1</td>
</tr>
<tr>
<td>A3</td>
<td>85.8</td>
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<tr>
<td>C1</td>
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<td>C1 mix</td>
<td>98.0</td>
</tr>
<tr>
<td>all others</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Conclusions

Self-assembled columns aligned with [010] result in debilitating reduction of Li transport in LiFePO\(_4\), while columns lacking alignment along [010] exhibit enhancement. The granular-scale transport limitations identified here yield important insights necessary to achieve optimal performance in thin and thick electrodes. The present theoretical results suggest two alternate development routes for high performance LiFePO\(_4\) cathodes: (1) mitigation of columnar order along [010] through introducing columnar frustrating additives or (2) reduction of the size of isometric nanoparticles and non-(010) nanoplatelets in pure systems. Incorporation of other multi-scale material development strategies with these approaches should enable the development of inexpensive, high performance LIB cathodes through material and process design informed by the findings of the present work.

Models and methods

Contact model and jamming

Jammed systems of frictionless particles represented by each shape in Fig. 1 are simulated at zero temperature (i.e., neglecting kinetic energy) via controlled consolidative and expansive strain with structural optimization at each strain step to find static equilibrium as in ref. 36 and 43. Cubic lattice periodic boundary conditions are employed to neglect wall effects; density \( \phi \) (i.e., solid volume fraction) is thereby computed as:

\[
\phi = \frac{\Sigma V_I/V_{cell}}{5} \tag{1}
\]

where the sum is over all particles \( I \) and \( V_I \) and \( V_{cell} \) are the volume of particle \( I \) and the volume of the primary periodic cell. Jammed structures are simulated by sequential compression of the periodic system from an initially dilute, random state at \( \phi = 0.005 \). The simulated structure thereby evolves with density via rearrangement simulated through structural energy minimization; the jamming sequence terminates after reaching stable static equilibrium near a pre-specified value of average energy \( E_t \). During the jamming sequence energy is minimized via the conjugate gradient method to average energy less than \( E_t \) or with a relative energy change convergence tolerance less than \( 10^{-12} \) at each strain step (see ref. 36). This minimization sequence ensures rapid convergence toward jammed structures. In some cases, systems are asymptotically expanded toward the jamming point to achieve convergence of jammed structural properties. For structural optimization, the conservative model employed for elastic contact between particles \( A \) and \( B \) results in a potential energy \( E_{AB} \):

\[
E_{AB} = \frac{1}{2} Y V^2 (V_A + V_B) \tag{2}
\]

where \( V \) is the intersection volume between the particles, \( V_A \) and \( V_B \) are the volumes of the respective particles in contact, and \( Y \) is elastic modulus. A target energy of \( E_t = 3.2 \times 10^{-5} Y V_p \) is employed in this work, where \( V_p \) is the number-weighted average particle volume. Convergence of structural properties with system size was considered. Most notably the size of systems of shapes C2 and C3 were increased to 400 and 200, respectively, to minimize the formation of percolating
columns – an artifact of finite system size. The binary system was composed of 100 C1 nanoplatelets and 640 additive icosahedra having a volume effective diameter of 1.5 [010]. 100 particle systems were considered in all other simulations.

Face–face contacts are identified, as in ref. 43, to characterize columnar ordering of jammed structures and to determine the extent to which electrolyte is restricted access to (010) faces. Accessible solid surface area for jammed systems is determined by computing the intersecting surface area of opposing faces projected onto the plane normal to the contact force of face–face contacts. Topological analysis of channel lengths is determined by performing two-dimensional geometrical boolean operations on faces projected onto column axes. Axes of individual columns were determined as the dominant eigenvector of the nematic tensor [see ref. 36] assembled with individual normal vectors of the (010) particle surfaces in a given column.

Lithium ion transport model

We model microstructures as distributions of one-dimensional planar shrinking core channels and consider the single-phase mode as a special case of the two-phase mode. Ion transport from electrolyte to the channels occurs in parallel and is coupled through galvanostatic and discharge kinetic conditions. In the present analysis we do not consider potential gradients in the electrolyte, and therefore the electrolyte possesses a spatially uniform, time varying potential $E$. Though electrolyte resistance can lead to potential gradients, we neglect it to isolate the effects of columnar ordering on diffusion in LiFePO$_4$. The galvanostatic discharge of a system of one-dimensional channels is simulated by the simultaneous solution of concentration fields in each channel subject to constant discharge rate per unit LiFePO$_4$ volume, $I$:

$$I = V_{tot} \sum_i j_{i,i} A_i,$$

where $F$, $V_{tot}$, $j_{i,i}$, and $A_i$ are Faraday’s constant, total LiFePO$_4$ volume, and ion surface flux and area of channel $i$ exposed to electrolyte, respectively. Coupling between channels occurs through solid-electrolyte surface reaction kinetics, which we model with Butler-Volmer kinetics having equal cathodic and anodic transfer coefficients: $58$

$$j_{i,i} = -i_0 \left[ \exp \left( \frac{0.5F}{RT} (E - E_0) \right) - \exp \left( -\frac{0.5F}{RT} (E - E_0) \right) \right].$$

where $i_0$ is the exchange current density, $E$ is the insertion potential felt by all exposed LiFePO$_4$ surfaces, and $R$ is the universal gas constant. Here we employ an exchange current density of $5.4 \times 10^{-5}$ A/m$^2$ experimentally determined by Dargaville and Farrell. $59$ We model the equilibrium potential $E_0$ in Volts as an empirical function:

$$E_0 = 3.4245 + 0.858e^{-800(c_{li}/e_{max})^{1.3}} - 17e^{-0.98(c_{li}/e_{max})^{14}},$$

where the maximum concentration of lithium $e_{max}$ in LiFePO$_4$ is 21,190 mol/m$^3$ (ref. 60), and $c_{li}$ is the concentration of lithium ions at the surface of channel $i$. For the two-phase mode each channel is modeled as a symmetric planar shrinking core with uniform ion concentration in the lithium-deficient $x$ phase equal to the equilibrium terminal miscibility $c_{li}^0$ [572 mol/m$^3$ in ref. 60]. For the single-phase mode the two-phase interface is pinned at the midpoint of each channel. For both modes ion concentration $c_i$ in the lithium-rich $\beta$ phase is governed by the diffusion equation:

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial y} \left( D_\beta \frac{\partial c_i}{\partial y} \right),$$

where $t$ is time and $y$ is the spatial coordinate along [010]. We utilize a value of $8 \times 10^{-18}$ m$^2$/s (ref. 54) for the diffusion coefficient of the lithium-rich phase $D_\beta$. The governing equation is subject to mixed boundary conditions:

$$-D_\beta \frac{\partial c_i}{\partial y} \bigg|_{y=0} = j_{i,i},$$

$$c_i|_{y=x_i(t)} = c_{i,i}^0,$$

where $x_i$ is the interface position in channel $i$, and $c_{i,i}^0$ is the terminal miscibility of lithium in the $\beta$ phase [18,010 mol/m$^3$ in ref. 60]. Symmetry of channels about their midpoint requires only half of the domain to be simulated. When interface position reaches the symmetry point in the channel (i.e., $x_i = L_i/2$) the interface cannot propagate further (e.g., in the case of the single-phase mode), and the constraint imposed by eqn (8) is no longer relevant. Mass balance on the $\beta$ phase yields an equation coupling interface position to the concentration field:

$$\frac{\partial}{\partial t} \left( \int_0^{x_i} c_i \, dy \right) = j_{i,i} + c_{i,i}^0 \frac{dx_i}{dt}.$$

For the two-phase conversion mode interface position is initially set to a small value, $x_i = t_0109 \times 10^{-3}$, with uniform concentration in the $\beta$ phase, $c_i = c_{i,i}^0$, while for the single-phase conversion mode interface position is held at its terminal position, $x_i = L_i/2$, and concentration is set initially to $c_i = c_{i,i}^0$.

We utilize the Landau transformation, $u_i = y/x_i$, to numerically solve eqn (6). $61,62$ This transformation converts the moving interface boundary condition [eqn (8)] to a fixed one with respect to $u_i$, but introduces a nonlinear advective term into the governing equation $59$ that can be manipulated into conservative form. We employ the conservative form of the transformed equations $61,62$ on which the finite volume method is used to discretize the governing equations. A fully implicit time-stepping scheme with central difference approximation of diffusive fluxes and upwind approximation of advective fluxes are employed.

In all simulations 50 mesh points are employed to discretize $u_i$ with a discharge rate dependent time step of $c_{max}F/(200I)$. For systems with particles having a contribution from continuously varying channel length (e.g., spheres and shape B) continuous distributions are sampled with 50 evenly spaced points per $t_0109$ to obtain discrete channel length distributions. The set of equations formed by the discretized diffusion equation, boundary conditions, and interface propagation rate for each channel are solved via adaptive interpolation of electrolyte potential $E$ with respect to total discharge current. The ion concentration $c_{li}$ of the LiFePO$_4$ surface exposed to
electrolyte was determined subject to a Neumann boundary condition of the ion surface flux \( j_{i,s} \). Twenty logarithmically-spaced guesses for the ion surface flux \( j_{i,s} \) were made to build interpolation functions for each channel between \( j_{i,s} \) and the time varying, spatially uniform electrolyte potential \( E \). Integrating flux over all channel surfaces, as in eqn (3), yields an interpolation function of discharge current per unit LiFePO₄ volume \( I \), which is then used to solve for electrolyte potential at the value of \( I \) specified by the galvanostatic discharge rate, \( nC \).

At a given time step variation of potential among all channels converges to within \( 10^{-10} \) Volts; convergence of the galvanostatic discharge rate was achieved within \( 1 \times 10^{-8} \).

**Appendix**

**Geometry of particle shapes**

The shapes of particles investigated are represented by convex polyhedra. Each shape possesses crystallographic symmetries of the olivine structure of LiFePO₄ because they represent single crystals. Provided in Table 3 is information about planar faces representing the entire family of planes bounding each shape; the remaining planes are reflections of the primary planar faces in Table 3 about \( x \), \( y \), and \( z \) axes. Vertex coordinates can thereby be found as the intersection of all planar half-spaces bounding a given shape.

Two small faces [(120) and (021)] appearing in the shape of ref. 32 do not appear in our Wulff construction of shape B, which we attribute to the finite precision of surface energies presented in that work. The third face that differs from that in ref. 32 is (221); this may likely be an error in the surface energies presented by Fisher and Islam, as they have presented another surface energy in the Supplementary Information of ref. 32 indicating (221) with higher surface energy.

**Notes and references**


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**Table 3** Geometric parameters describing LiFePO₄ particle shapes considered in the present work. \( x_i \), \( y_i \), and \( z_i \) represent the components of the outward-pointing unit normal vector for primary planar face \( i \) of a convex polyhedral particle. \( d_i \) represents the distance from the center of the particle from planar face \( i \) projected along the unit normal vector of that face. \( t_{[010]} \) is the thickness of a given shape in the [010] crystallographic direction.

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<th>Shape A3</th>
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