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Preview

The Secret Life of $LiFePO_4$ Particles

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In a recent issue of *Nature Materials*, Yiyang Li, Saiful Islam, Martin Bazant, William Chueh, and colleagues identify the major role of solvent-assisted lithium migration in $LiFePO_4$ particles along the solid/liquid interface using a combination of X-ray diffraction, microscopy experiments, and *ab initio* molecular dynamics simulations. This finding suggests that at the particle scale $LiFePO_4$ effectively becomes a three-dimensional Li conductor, and follow-up phase-field simulations suggest that lowering surface diffusivity is a predominant factor in determining the bulk phase transformation behavior during cycling.

Poring through the vast and growing volume of energy research literature, we see continual progress toward mitigating some of the defining challenges of our time through the interplay of basic science and applied studies.[1] While insight-driven studies are designed to rationally inform the next breakthrough in device performance, the reverse sequence also occurs with regular frequency, where an unexpected result demands further fundamental investigation to unearth the origin of improved performance.

The now multi-decade research effort on $LiFePO_4$ (LFP) cathode materials embodies this chicken-and-egg relationship between optimizing device performance and understanding underlying mechanisms. Goodenough, Padhi, and colleagues introduced LFP as a new cathode material for lithium-ion batteries (LIBs) in 1997,[2] and their study accurately characterized most of the defining properties of the material: open-circuit voltage of 3.4 V versus Li metal, ordered olivine crystal structure, reversible Li intercalation with 170 mAh/g theoretical capacity, excellent stability and cycle life, and notably, strong Li phase separation at room temperature. Based on this last feature, the authors concluded that, while promising, LFP would be relegated to low-rate applications due to the inherent kinetic barriers imposed by maintaining two-phase coexistence within the active particles during cycling.

In the 2000s, however, not only did researchers demonstrate that extraordinarily high cycling rates could be achieved while retaining a significant fraction of the theoretical capacity,[3–5] but LFP also gained traction across the globe as a robust and commercially viable electrode material for a variety of industrial applications. LFP batteries are reliably used today in cordless power tools, vehicles (considered as a replacement for lead-acid batteries), and specific stationary storage applications, just to name a few of its wide-ranging uses.

A significant part of the appeal of LFP, alongside high rate-performance, is its built-in safety and ability to endure several thousand charge and discharge cycles without significant deterioration in performance, all without reliance on resource-constrained critical metals.[6,7] Barring its lower voltage (3.4 V compared to 4 V) compared to layered cathode materials, which are used to power portable electronics and electric vehicles (but suffer from their own limitations, namely safety and quicker degradation), LFP is considered an "almost perfect" electrode material for LIBs.

So what are the fundamental atomic-scale mechanisms that endow LFP its remarkable rate-performance? Following Goodenough's seminal work, ensuing studies revealed that there is indeed rapid Li diffusion, albeit in only one crystallographic direction in the olivine structure. Also, computational and experimental studies suggested and confirmed that phase separation within a LFP particle could be suppressed during charging and discharging. Instead, with modest overpotential particle (de)lithiation can proceed through a non-equilibrium solid-solution pathway, and then relax to an interparticle or intraparticle two-phase equilibrium when the applied potential is removed.

Still, a perplexing question remains: the stable phase boundaries observed within LFP particles in the equilibrium state are perpendicular to the crystallographic directions that correspond to almost non-existent Li diffusion, so how does lithium migrate during the solid-solution to two-phase transformation? In a recent issue of *Nature Materials*, Yiyang Li, Saiful Islam, Martin Bazant, William Chueh, and colleagues identify the major role of solvent-assisted lithium migration along the solid/liquid interface without leaving the active particle, using a combination of X-ray diffraction, microscopy experiments, and *ab initio* molecular dynamics simulations.[8] This finding suggests that at the active particle scale, LFP effectively becomes a three-dimensional Li conductor, and follow-up phase-field simulations suggest that

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lowering surface diffusivity is a predominant factor in determining the bulk phase-transformation behavior during cycling.

The authors first perform a systematic study elucidating the relaxation behavior of solid-solution $Li_{0.5}FePO_4$ microplatelet particles in different environments. Particles are lithiated at a rate of 1C–2C (meaning full charge or discharge in 30–60 min) to drive the particles into the solid-solution state, and the solid-solution fraction is monitored over time. In inert argon atmosphere, carbon-coated $Li_{0.5}FePO_4$ retains significant solid-solution character for hundreds of hours, and uncoated particles also demonstrate this behavior for 100 hr. However, in standard LIB solvent (ethylene carbonate and dimethyl carbonate, EC/DMC), ambient air, and argon/H_2O environment, the particles relax to the phase-separated state one to two orders of magnitude faster. *Ab initio* molecular dynamics simulations confirm that both EC and H_2O molecules present at the solid/liquid interface coordinate Li and assist migration from one fast-diffusing channel to the next, but no such Li surface transport occurs in vacuum environment, consistent with the experimental observations.

The relaxation behavior is then measured in electrolyte (1 M $LiClO_4$ in EC/DMC), and now particles are permitted to redistribute Li between other LFP particles to lower the global free energy (e.g., interparticle redistribution). Whereas surface Li migration does not require crossing the electrochemical double layer, interparticle Li redistribution requires a charge-transfer reaction step. Here the solid solution fraction decreases rapidly, but for the most part, Li is confined within the same particle during phase separation before interparticle Li redistribution takes effect at longer timescales, ultimately resulting in a population of fully lithiated and fully delithiated particles.

Finally, the authors integrate their observations and perform phase-field simulations to model phase separation during constant current conditions while taking into account the effects of surface diffusion. As the surface diffusivity increases, so too does the threshold current density required to sustain a bulk solid-solution transformation pathway. By identifying the outsized role of surface Li diffusion in LFP electrodes, a new kinetic consideration is identified that links mechanistic understanding back to device performance, with resounding implications for the broader class of anisotropic phase-transformation systems where phase boundary propagation and bulk ion diffusion directions are orthogonal.

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