MATERIALS SCIENCE

Building a Better Battery

Controlling the charge-induced morphological changes of electrode materials may provide a route to improved battery performance.
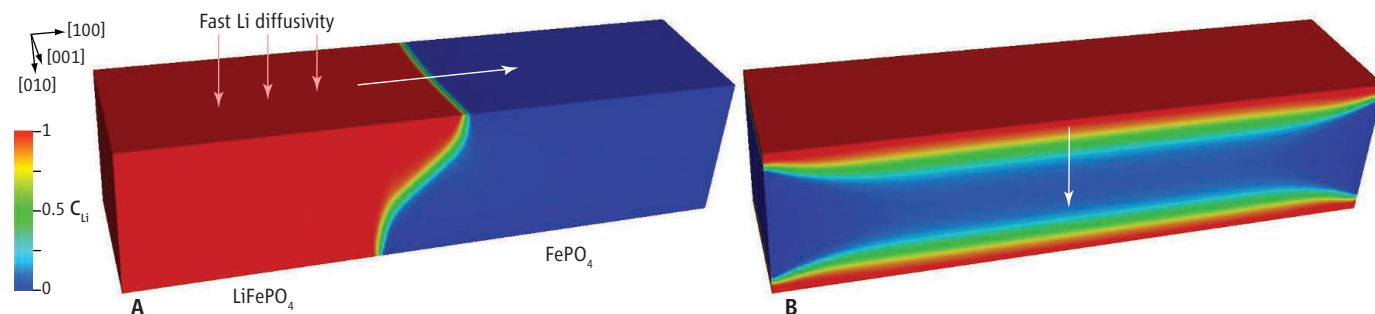
Yet-Ming Chiang

Innovations in the battery field are infrequent and hard-won. New electrochemical systems (a new positive or negative electrode, electrolyte, or combination thereof) reach the marketplace only once every few years, and the energy density of lithium-ion batteries as a class has increased on average by only 8 to 9% per year since the early 1990s. Thus, in the burgeoning field of nanoscale electrode materials, skepticism regarding new claims is perhaps not surprising because of the many requirements that any battery electrode must simultaneously meet to be commercialized. One route by which battery performance can be com-

cerns specific to nanomaterials: Nanoparticle electrodes may have low packing density that makes high bulk energy density difficult to realize; synthesis methods may not be scalable and/or economical in a field where cost is a most important metric (e.g., electric vehicle and grid storage batteries); and nanoscale forms of inherently reactive compounds raise questions of safety and stability. There are also fundamental scientific questions centered on the mechanisms of electrochemical storage because of departures from known scaling laws as the size scale decreases. All of these issues need to be convincingly and simultaneously addressed if laboratory-based

Li_2O or LiF that does react reversibly with the metal electrode and is the main contributor to reversible capacity (*2*, *4*). However, the large strain accommodation capability shown by the SnO_2 nanowires would be valuable if achievable in other high-capacity, high-strain electrodes such as silicon. Alloying with Li to the limiting composition $Li_{4.4}Si$ yields theoretically an enormous capacity of 4200 milliampere hours per gram (mAh/g), versus 150 mAh/g for $LiCoO_2$ cathodes and 350 mAh/g for graphite anodes used in conventional lithium-ion batteries, but also produces a molar volume change of 311%. Silicon undergoes solid-state amorphization during lithiation

Coping with strain. (**A**) Phase field modeling reveals that under a moderate overpotential of 25 mV, misfit stress causes $FePO_4$ to grow along the [100] longitudinal direction, normal to the fast-diffusion direction. (**B**) Increasing the overpotential to 100 mV allows Li diffusion anisotropy to dominate the transformation morphology; diffuse phase boundaries migrate inward along the [010] direction. C_{Li}, lithium concentration

promised is by mechanical failure due to the large volume changes associated with the charge-discharge cycle. On page 1515 of this issue, Huang *et al.* (*1*) report an ingenious in situ transmission electron microscope (TEM) experiment that uses a low–vapor pressure ionic liquid electrolyte to allow imaging of a SnO_2 nanowire electrode in an "open" electrochemical cell. They observe a reaction mechanism in the SnO_2 nanowires that progresses sequentially along the nanowire from end to end, allowing them to accommodate a ~250% volume change without fracturing and at practical charging rates. These intriguing results raise the question of whether such one-dimensional phase transformations can be induced in other materials.

Nanomaterials offer the promise of high storage capacity at useful current rates, along with reversible cycling over hundreds to thousands of cycles and over a wide temperature range. However, there are practical con-

results are to be successfully translated into substantial progress in battery performance.

SnO_2 is a model for a class of metal oxides and fluorides (*2*–*4*) in which reversible storage capacities exceeding those possible with intercalation reactions are realized with displacement or "conversion" reactions that produce one or more new phases. Electrochemical reduction of the starting oxide by lithium produces Li_2O [LiF in the case of the fluorides (*4*)] and the parent metal, but unlike primary battery systems such as Li/MnO_2 that undergo the same reaction but are poorly reversible, reversible storage has been obtained when the product phases are nanoscale and reactive. In the case of SnO_2, the Li_2O reaction product does not participate in reversible storage; subsequent cycling stores lithium through an alloying reaction with the nanoscale particles of metallic Sn. This was first established in SnO_2-bearing glasses (*5*) and is also the case for Huang *et al.*'s nanowires. Thus, this reaction mechanism has the drawback of a large and irreversible loss of working lithium in the first cycle, whereas in other systems the conversion reaction produces nanoscale

(*6*), and one strategy for strain accommodation is to limit the extent of lithiation (which sacrifices charge storage capacity) to maintain an amorphous phase (*7*). Silicon nanowires, on the other hand, have exhibited reversible capacities exceeding 3000 mAh/g (*8*).

In considering how one-dimensional transformation morphologies might be induced, an example from the first successfully commercialized nanoscale cathodes, the phospho-olivines, may be instructive. Strain accommodation (*9*, *10*) and related phase transformation kinetics (*11*) are tunable features of nanoscale olivines and have been implicated as design criteria for high-power and long cycle life. The figure shows results using a phase-field model (*12*) to simulate possible transformation morphol-

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ogies in a LiFePO$_4$ nanorod during the first-order phase transition to FePO$_4$. The anisotropy of Li diffusion and the magnitude of misfit strain (~7% volume strain) have been explicitly included, and the driving force for the transformation is varied via the electrical overpotential (13). At a moderate overpotential of 25 mV (see the figure, panel A), stress relaxation causes FePO$_4$ to grow along the [100] longitudinal direction, analogous to that of Huang et al., even though Li diffusion is fastest normal to this direction. However, at a higher overpotential of 100 mV, the influence of strain energy is overcome and lateral Li diffusion dominates the transformation morphology (see the figure, panel B).

Thus, interactions among stress, transport anisotropy, and the magnitude of the driving force (among other variables) may influence

phase transformation morphology in nanowire electrodes. Other unanswered questions include the effect of electrolyte distribution: Is the one-dimensional transformation in SnO$_2$ facilitated by having a thin wetted layer of electrolyte, and would results differ for a "flooded" electrolyte battery? And could a competing radial reaction morphology also preserve the nanowire morphology? Regardless, the results presented by Huang et al. are testimony to the power of direct observation in electrochemical materials science, and they illustrate a previously unrecognized mode of reaction in battery electrodes. The results should stimulate others to consider analogous experiments and mechanisms in other storage materials, and should contribute to the design of nanoscale electrodes that fully exploit the potential of ultrahigh-capacity storage materials.

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PLANT SCIENCE

Genome Evolution in Plant Pathogens

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Pathogen genes that shut down specific host plant immune responses are highly divergent and have evolved rapidly to accommodate adaptation.

Food security is of global importance and crop diseases caused by plant pathogens are a major constraint to agriculture worldwide. Many of these pathogens have a similar biotrophic life stage during which they contact host cells and secrete effector proteins that alter plant responses to infection (1). In this issue, comparative genomics studies of closely related pathogen species by Raffaele et al. on page 1540 (2), Baxter et al. on page 1549 (3), Spanu et al. on page 1543 (4), and Schirawski et al. on page 1546 (5) reveal that such effector proteins evolve rapidly and that their diversity contributes to host range and parasite speciation.

Biotrophic infection strategies have evolved independently in diverse lineages of plant pathogens. These include fungus-like parasites (oomycetes) from the kingdom Stramenopila, such as the destructive potato blight pathogen *Phytophthora infestans* (agent of the Irish potato famine), fungi such as powdery mildews (ascomycetes), and rust and smut fungi (basidiomycetes). These pathogens form specialized hyphae (called haustoria) that penetrate the plant cell wall

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Agricultural threats. Many pathogens, such as *Phytophthora infestans*, target major food crops, such as potato (shown). The genes involved in host-pathogen interactions are highly diversified among related *Phytophthora* species that attack different plants.

and allow nutrient uptake from host tissue (6). These structures also secrete large repertoires of effector proteins that enter host cells and manipulate defense responses and cellular metabolism. Many oomycete effectors require the short amino acid motif RxLR (Arg, any amino acid, Leu, Arg) for entry into plant cells (7), independently of other pathogen machinery (8, 9). Some fungal effectors also enter host plant cells (10, 11), although they lack clearly conserved peptide motifs.

Raffaele et al. compared the genomes of four very closely related *Phytophthora* species that infect quite different host plant species (see the figure). The evolution of these

pathogens therefore involved relatively recent shifts in host range, followed by specialization to the new hosts. They found most pathogen genes and genome regions to be highly conserved, but genes involved in host-pathogen interaction appear highly diversified, especially the predicted RxLR-containing effectors. Most of these genes are located in gene-sparse, transposon-rich genome regions, suggesting that these features allow rapid evolution of effector loci after host changes. Genes involved in chromatin modification are also located in these regions and show extensive variation, suggesting that epigenetic regulation of gene expression also contributes to adaptation following host shifts.

Despite having a biotrophic life stage, *Phytophthora* species subsequently kill the infected parts of the plant but continue to feed on the dead plant tissue (and can be cultured on simple medium). By contrast, the related oomycete *Hyaloperonospora arabidopsidis*, which is a pathogen of the model plant *Arabidopsis thaliana*, is exclusively biotrophic and cannot be grown in culture. This pathogen is believed to have evolved from a *Phytophthora*-like hemibiotrophic ancestor. Baxter et al. found that its genome contains a unique set of diversified RxLR-containing effectors but has lost many of the hydrolytic