Preserving order by controlled disorder

Timo Boehler & Dominic Bresser

Nickel-rich lithium-ion cathode materials face severe structural and interfacial instabilities when cycled at high potentials and high degrees of delithiation. Now, a $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ material with a complementary composition and structure gradient, composed of an ordered, layered Co-poor bulk phase and a Co-enriched disordered rock-salt surface layer, is shown to efficiently address the issues.

An ambitious objective in battery research is to enhance lithium-ion batteries (LIBs) by pushing the limits of capacity and operating potential ($\geq$4.5 V versus Li^+/Li) of cathode active materials, while ensuring safety and long-term cyclability. This is particularly challenging, as highly nickel-rich layered $LiNi_{1-x-y}Mn_xCo_yO_2$ (NMC) cathode materials, the current state of the art for high-energy LIBs, suffer from serious structural and interfacial instabilities when cycled to high potentials (>4.3 V versus Li^+/Li) and high degrees of delithiation[1,2].

To mitigate these limitations, various strategies are under investigation, including bulk doping, core–shell structures with transition-metal concentration gradients, surface engineering via coatings, and the design of functional electrolyte additives[2–5]. Nevertheless, addressing the interplay of intrinsic structural instability, accompanied by morphological degradation and particle cracking as well as parasitic surface reactions remains highly challenging.

In this context, writing in *Nature Energy*, Tongchao Liu, Khalil Amine, and colleagues[1] from Argonne National Laboratory and Brookhaven National Laboratory report a highly effective, dual-gradient particle design of $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811). Their approach features a concentration gradient from a cobalt-poor core to a cobalt-enriched surface and a complementary structural gradient, with the conventional ordered layered structure in the particle bulk transitioning to a stable yet electrochemically active disordered rock-salt surface layer (Fig. 1). This combination results in remarkable cycling stability even at elevated cut-off voltages of up to 4.7 V versus Li^+/Li and high capacities, while minimizing lattice strain, irreversible phase transformations, and surface degradation.

Specifically, the material presented by Liu, Amine, and team achieves a high first discharge capacity of 226 mAh g^{-1} at a low current density with an upper cut-off voltage of 4.5 V, matching the performance of a reference NMC811 material. Also, when increasing the charge/discharge rate, the material still performs as well as, if not better than, the reference material at high rates, despite the incorporation of the disordered phase at the particle surface, which would typically result in a reduced rate capability. The foremost benefit of the gradient design is evident upon constant current cycling, with negligible capacity fading over the tested number of cycles in Li-metal cells, compared to an 88% capacity retention for the NMC reference cell. Remarkably, at the upper cut-off voltage of 4.7 V, the material retains 92% capacity versus 82% for the reference cell.

Notably, this seemingly complex particle design was realized using a comparatively straightforward and scalable synthesis approach. A transition-metal hydroxide precursor was prepared by a conventional two-step coprecipitation process, followed by high-temperature calcination. The precursor was initially composed of a core–shell particle with a Co-poor bulk and a Co-enriched surface. Contrary to the
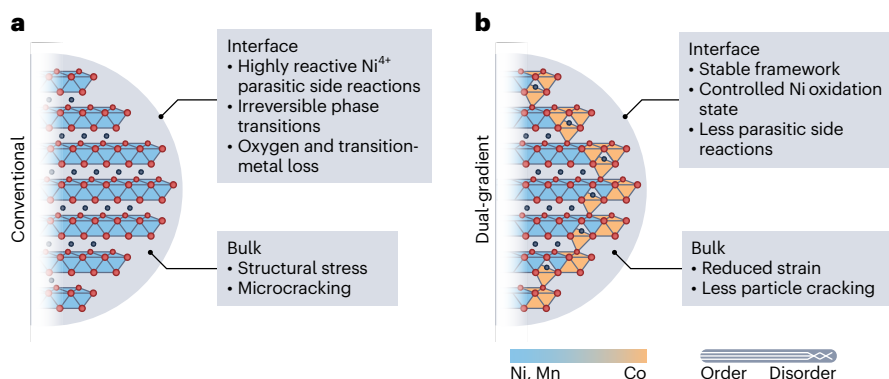
Fig. 1 | The dual-gradient modification strategy. a, Schematic illustration of a conventional layered oxide and the typical degradation pathways related to its structural instabilities. **b**, Schematic illustration of the presented dual-gradient material, composed of an ordered Co-poor bulk phase and a Co-enriched disordered rock-salt surface layer, and the resulting advantages. The colour coding indicates the prevalent elemental distribution of Mn and Ni (blue) and

Co (red), while the transition from an ordered to a disordered phase is schematically illustrated by the intermixing of Li (the grey dots) and the transition-metal layers in the near-surface region. This is also depicted in a highly simplified manner (schematically illustrated at the bottom) by sketching the transition from a layered (ordered) structure to an intermixed (disordered) structure.

expectation of a simple concentration gradient, a structural gradient from an ordered to a disordered phase was observed. Liu, Amine, and colleagues suggest that this effect might result from the significant Co concentration differences and the consequently strong inter-diffusion.

The research team provides detailed insights into the underlying mitigation mechanisms. First, the disordered rock-salt phase offers a rigid and densely packed structural framework that limits and alleviates the bulk structural stress, especially towards the end of the charge process. As a result, morphological degradation and microcracking are significantly reduced, minimizing the exposure of fresh and vulnerable surfaces to the electrolyte.

Second, the nickel redox activity within the disordered rock-salt phase differs from the ordered phase in the bulk, with nickel oxidation states generally remaining lower in the disordered phase, which suppresses electrolyte oxidation at high potentials. Nonetheless, the disordered rock-salt phase remains electrochemically active, which is in sharp contrast to the typically inactive degradation-type rock-salt phase that forms upon cycling[2]. Liu, Amine, and colleagues conclude that the suppressed exposure of Ni^{4+} at the particle surface effectively shields the electrolyte from severe parasitic side reactions, including oxygen loss, transition-metal dissolution, and irreversible surface reconstruction[2,6,7].

With their work, Liu, Amine, and team provide a compelling perspective on the design of core–shell NMC cathode materials, extending beyond the well-established concept of concentration gradients. They highlight the potential of the disordered rock-salt phase as a structurally coherent and integrated protective surface layer. We note, however, that the thickness of this layer is crucial, likely requiring an optimum balance to maximize the lithium diffusivity and capacity.

Their study also raises two interesting questions for future research. First, can this approach be extended to higher nickel concentrations beyond the 87% demonstrated in their active material, providing even higher energy density while stabilizing the interface with the electrolyte and improving thermal stability and safety?

Second, how might the composition of the disordered rock-salt phase be further optimized?

Disordered rock-salt phases that are electrochemically active commonly rely on the inclusion of d^0 elements to stabilize the formation of the disordered structure and on excess lithium to modulate the lithium diffusivity[8]. Liu, Amine, and team challenge these norms with a 'simple' NMC composition and standard synthesis conditions. Further research might be needed to better understand and control the formation and the composition of the disordered near-surface phase to enhance physicochemical and electrochemical properties, and ideally, to avoid cobalt.

Nonetheless, Liu, Amine, and colleagues show that this material design strategy, which goes beyond classic approaches such as doping and surface coatings, holds great promise for advancing the lifetime and energy density of lithium batteries. This highlights once again that there is still "plenty of room at the bottom"[9].

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