Lithium-ion Batteries

Entropy-assisted epitaxial coating

Simon Schweidler, Torsten Brezesinski* & Ben Breitung*

Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany

* *Corresponding authors:* torsten.brezesinski@kit.edu, ben.breitung@kit.edu

Surface reconstruction, chemo-mechanical degradation, and interfacial side reactions are major factors limiting the cyclability of Ni-rich cathodes. A new strategy based on entropy-assisted epitaxial coating is shown to effectively mitigate these issues, leading to improved battery performance and promising advances in electrochemical energy storage.

The increasing technologization of society, combined with the transition to renewable energy sources and the widespread adoption of electric vehicles, is driving the demand for rechargeable batteries with high energy and power densities. Current Li-ion batteries utilizing layered oxide cathode active materials (CAMs) based on cobalt, nickel, manganese, or aluminum face cycling instabilities, particularly at high operating voltages and charging rates. Overcoming these challenges is crucial for enhancing performance and advancing applications. Additionally, efforts are being made to reduce cobalt usage due to ethical, environmental, and cost concerns. Therefore, research on high-performance batteries is largely focusing on Ni-rich (Co-poor) CAMs, but they also grapple with the aforementioned challenges.

The low stability of Ni-rich cathodes is often linked to structural degradation, as well as to stress and strain effects, leading to particle fracture and undesired interface/interphase formation, hindering electron and/or ion transport. Writing in *Nature Energy*, Khalil Amine and colleagues in the USA and China present an entropy-assisted epitaxial coating method for Ni-rich CAM particles with a multicomponent material, significantly improving performance by reducing surface reconstruction and strain propagation during cycling.[1]

The key to enhanced performance lies in the protective coating material, which adopts a Wadsley-Roth structure ($Nb_{12}WO_{33}$). This structure comprises polyoxometalate blocks ordered in different ways, providing pathways for fast ion transport. Amine and colleagues coated a nanoparticulate mixture of $Nb_{12}WO_{33}$ and ZrO_2 onto the surface of a $LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$ (NCM90) CAM via high-speed mixing, followed by annealing at 700 °C. They showed that some transition metal elements from the NCM90 migrated

into the surface layer, reacting with the nanoparticulate mixture during heating and consequently forming a new phase aligned along the CAM's layering direction.

Multiple elements — W, Nb, Zr, Co, Ni, and Mn — are incorporated into the epitaxially grown coating on the NCM90 particles, thereby increasing the configurational entropy. Literature reports indicate that an increase in configurational entropy can lead to the merging of different crystal structures, eliminating phase boundaries and forming a single-phase compound. In their work, Amine and team showed that the orientation of the structure along the crystal planes of NCM90, induced by the epitaxial growth of the new phase, allows the coating to shield the surface of the active material while ensuring diffusion pathways for charge transport (Figure 1). They coined the term, entropy-assisted epitaxial coating, for this process.

High-entropy materials (HEMs) are gaining attention for application in batteries and other energy and electronic systems. HEMs represent compounds where at least five different elements (with concentrations ranging from 5 to 35 atomic%) occupy the same crystallographic site and are characterized by a configurational entropy (the part of entropy increasing with an increasing number of constituent elements) of at least 1.5*R* (*R* being the ideal gas constant). These materials have been reported to improve electrode performance by preventing degradation by making use of their intrinsic features like cocktail effects, lattice distortions, compositional flexibility, and structural stabilization.[2-4]

It is important to note that the threshold of 1.5*R* was empirically set to distinguish HEMs from compositionally less complex materials. However, cocktail effects arising from interactions between different incorporated elements may still occur with lower configurational entropies, as seen in the work of Amine and colleagues.[1] Although their electrode material may not necessarily meet the condition of being a HEM, the entropy effects help counteract structural degradation, thereby increasing battery stability. Nevertheless, further study is warranted to explore the origin of the stabilizing role of compositional disorder in the coated NCM90.

It is worth mentioning that in a recent study, Zhang *et al*. reported that doping $LiNi_xMn_yO_2$ with Ti, Mg, Nb, and Mo produces a quasi-strain-free CAM ($LiNi_{0.8}Mn_{0.13}Ti_{0.02}Mg_{0.02}Nb_{0.01}Mo_{0.02}O_2$), a material undergoing negligible volume change upon cycling while also staying well below 1.5*R*.[5] In this sense, the study by Amine and colleagues extends the high-entropy doping concept to coat industrially relevant CAMs, aiming to address the root causes of cycling-induced material changes. All these mentioned studies share the use of the high-entropy concept to engineer the bulk and/or surface properties of electrode materials, ultimately aiming at improving battery life, safety, and sustainability. Similar works on liquid and solid electrolytes and other (electronic) materials are available in the literature.[6–10]

The epitaxial growth of the coating significantly mitigates electro-chemo-mechanical degradation and improves ion-transport kinetics. Amine and team reported much-

improved cyclability in coin- and pouch-type Li half-cells. For example, after 200 cycles at a rate of 1C, the surface-modified NCM90 exhibits a specific capacity and capacity retention of 187 mAh/g and 96%, respectively, in contrast to the uncoated NCM90, which showed 138 mAh/g and 79%, respectively.

Taken together, following this strategy might pave the way toward the development of advanced battery materials. Additionally, HEMs, as well as multi-elemental doping or coating, offer the possibility of tailoring properties to meet specific needs through compositional design. The exclusion of certain elements, such as cobalt, can have adverse effects on cycling performance. However, overcoming these challenges by leveraging cocktail effects or lattice stabilization offers a potential solution for addressing general issues in future CAM generations. Therefore, the approach of utilizing HEMs, multicomponent materials, or complex doping for energy applications appears highly promising and could lay the foundation for a new era in battery technology.

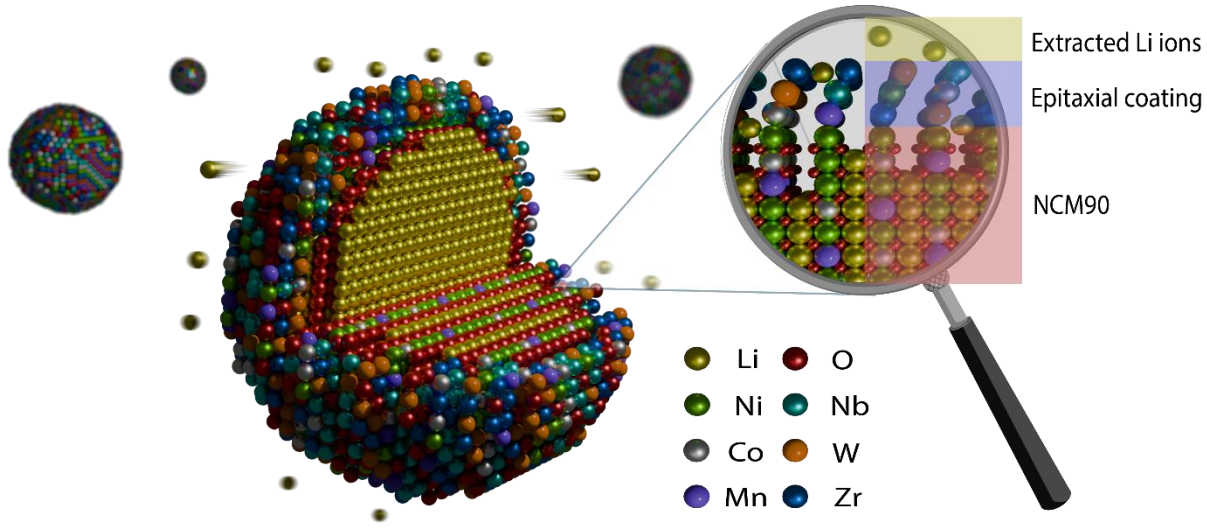

Figure 1: **Simplified illustration of the coated NCM90 particle**. The coating process involved high-speed mixing with $Nb_{12}WO_{33}$ and ZrO_2. As the NCM90 particle underwent heating, Co, Mn, and Ni diffused from the NCM90 into the coating layer, initiating the formation of a multicomponent phase that aligns epitaxially with the NCM90 surface, as seen more clearly in the magnified view. This entropy-assisted epitaxial coating preserves the layered structure of NCM90 and facilitates the rapid diffusion of Li while safeguarding the NCM90 surface from the electrolyte.

Competing interests

The authors declare no competing interests.

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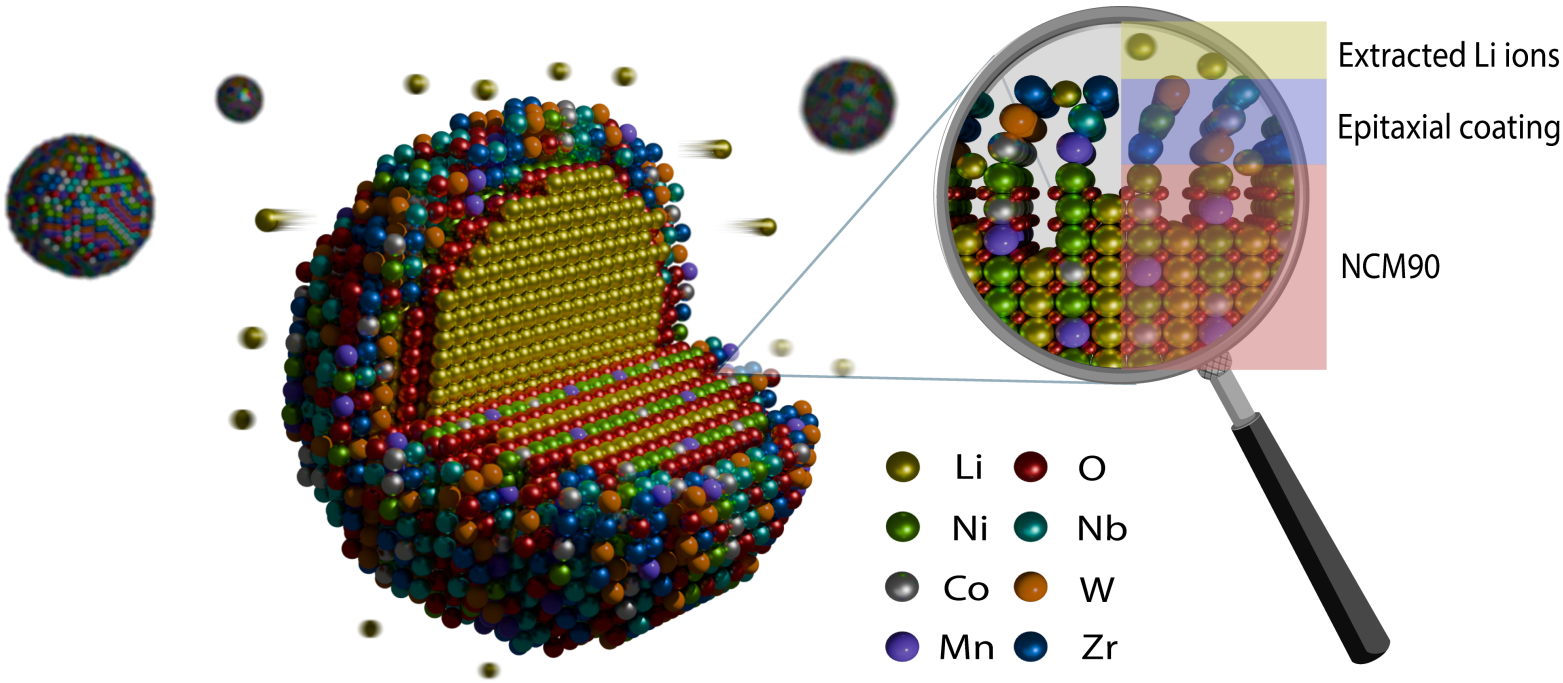
Extracted Li ions
Epitaxial coating
NCM90
Li
O
Ni
Nb
Co
W
Mn
Zr