Reversing planar gliding, microcracking enhances performance of single-crystalline Ni-rich cathode

In the quest to improve Li-ion batteries for electric vehicles, researchers have turned their attention to increasing the nickel content of the cathode. The primary motivation was to reduce phase boundaries and materials surfaces to address the challenges present in its polycrystalline counterpart (lithium-ion batteries). Nickel-rich cathode materials (NMC) are widely available at low cost, have low toxicity compared to other battery materials, and store more energy. However, despite Ni-rich cathodes deliver more energy, last longer, and are less expensive, the synthesis of

high-performance single-crystalline Ni-rich cathodes is challenging. A research group led by Jie Xiao of Pacific Northwest National Laboratory and the University of Washington now reports characterization studies of this material. The most common NMC is polycrystalline and comprises an aggregate of many nanocrystals. This structure can be damaged after repeated cycling, resulting in intergranular cracking on the surface. The surface exposure to electrolytes can also accelerate unwanted side reactions, increase moisture sensitivity, and generate gas.

As reported in a recent issue of *Science* (<https://doi.org/10.1126/science.abc3167>), Xiao's group used high-performance single-crystal NMC76 (nickel-rich cathode material #76) to

study the structural changes undergone by single crystals and their effects on the electrochemical properties of the cathodes. The electrochemical performance of the NMC76 crystal lattice showed that the gliding of the single-crystalline NMC76 lattice occurred at high voltages (see **Figure**). Microcracks were also observed, but gliding is the primary degradation mechanism of single crystals of NMC76.

The researchers found that repeated gliding will eventually cause a microcrack to form that exposes the surface to the electrolyte. By analyzing the NMC76 crystals with scanning transmission electron microscopy, the researchers were able to observe that the microcracks originate inside the crystal. Xiao's group studied the sliding process back and forth during 120 cycles and did not identify microcracking in the single crystal; for that reason, they suggested that this gliding and cracking can be reversible after 120 cycles.

The findings show that reducing the crystal size to less than 3.5 μm , optimizing the depth of charge that is the electrical energy stored in a battery by charging that was recovered by discharging at a certain point of time, and absorbing accumulated strain energy by modification of the structure symmetry can stabilize single crystals of NMC with little effect on their ability to be cycled reversibly.

Joan Stephanie Torres-Rodríguez

(a) Scanning transmission electron microscope (STEM) cross-sectional bright-field image of single-crystalline NMC76 after 200 cycles. (b) Bright-field STEM image of internal slicing. Credit: *Science*.