

Coherent X-ray Diffractive Imaging of Topological Defects in Operando Energy Storage Materials

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Attempts to produce focusing x-ray optics date back to the days of Roentgen, however, it was not until the past decade that X-ray Microscopy has finally been able to achieve sub-100 nm resolution.

We developed lensless x-ray microscopy techniques, which rely on coherent properties of x-ray beams, and eliminate the need for focusing optics altogether, replacing it with a computational algorithm. We have applied these techniques to image the distribution of lattice strain in wide range of nanostructures. Lens-less imaging, also known as Coherent X-ray Diffractive Imaging (CXDI) technique is especially powerful in Bragg scattering geometry (see Fig. 1) for in-operando imaging of lithium ion diffusion and dislocation dynamics in lithium ion energy storage devices.

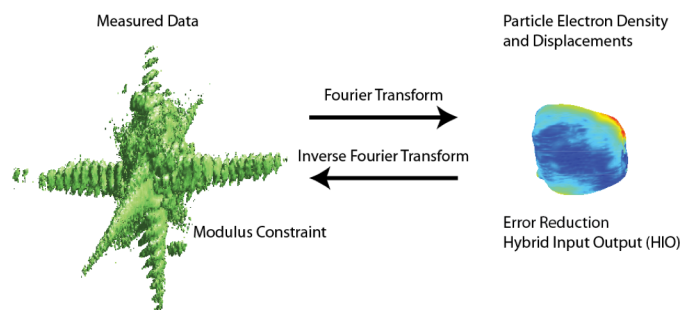


Fig. 1. Bragg CXDI approach involves solving for missing x-ray phases using iterative phase retrieval algorithms.

Topological defects can markedly alter nanomaterial properties. This presents opportunities for “defect engineering,” where desired functionalities are generated through defect manipulation. However, imaging defects in working devices with nanoscale resolution remains elusive. We report three-dimensional imaging of dislocation dynamics in individual battery cathode nanoparticles under operando conditions

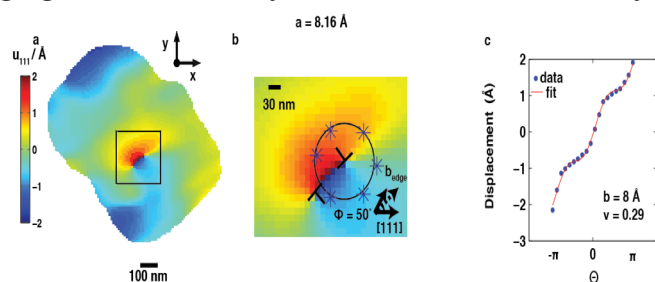


Fig. 2. (a) and (b) Edge dislocation displacement field identified in a single LNMO cathode nanoparticle. (c) Displacement field profile around dislocation core (circular path shown in (b)) matches expected behavior for edge dislocations.

using Bragg coherent diffractive imaging (see Fig. 2). Dislocations are static at room temperature and mobile during charge transport. During the structural phase transformation, the lithium-rich phase nucleates near the dislocation and spreads inhomogeneously. The dislocation field is a local probe of elastic properties, and we find that a region of the material exhibits a negative Poisson’s ratio at high voltage. Operando dislocation imaging thus opens a powerful avenue for facilitating improvement and rational design of nanostructured materials.

I will also discuss our recent results regarding defect dynamics in Lithium-rich layered oxides (LRLO). The LRLO material is a composite of a classical layered oxide LiTMO_2 (with $R\bar{3}m$ space group, TM

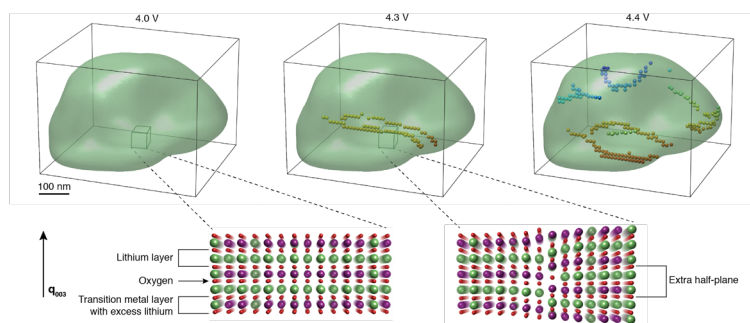


Fig. 3: Formation of a dislocation network during charge. Isosurface rendering of a LRLO particle measured in operando during charge. At a charge state of 4.0 V vs Li^+ no dislocations are observed in the particle. At 4.3 V two edge dislocations have formed during lithium extraction (shown by dotted lines in the particle) and at 4.4 V a dislocation network emerges (colors are used to represent different dislocations).

activity affects the structural long-term stability remains incomplete. Here, using operando three-dimensional Bragg coherent diffractive imaging, we directly observe the nucleation of a mobile dislocation network in LRLO nanoparticles. The dislocations form more readily in LRLO as compared with a classical layered oxide, suggesting a link between the defects and oxygen redox activity (see Fig. 3). We show microscopically how the formation of partial dislocations contributes to the voltage fade, a long standing issue hinders the practical use of this group of materials.

By measuring the length of dislocations in single nanoparticles, we directly calculate the dislocation density to be $1 \times 10^{10} \text{ cm}^{-2}$ in LRLO at 4.4 V (note that in traditional energy storage materials this density is approximately one order of magnitude smaller). At such a high value, we anticipate a sizable impact on the material's performance, particularly on voltage fade and oxygen activity. Although the strain energy is negligible to the total capacity of the fully charged material, the nucleation of line defects dramatically modifies the local lithium environment through perturbing the sequence of oxygen layers.

The new insights allow us to design and demonstrate an effective method to recover the original high voltage functionality. Our findings reveal that the voltage fade in LRLO is reversible and call for new paradigms for improved design of oxygen-redox active materials.

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stands for Ni, Mn, Co) and Li_2TMO_3 (with $C2/m$ space group). LRLOs are among the leading candidates for the next generation cathode material for energy storage, delivering 50% excess capacity over commercially used compounds. Despite excellent prospects, voltage fade in LRLO has prevented effective use of the excess capacity: a major challenge has been the lack of understanding of the mechanisms underpinning the voltage fade. Oxygen-redox reactions are believed to be responsible for the excess capacity; however, a mechanistic understanding of how the anionic