Ptychographic Phase Imaging of Heavy and Light Atoms in Battery Materials

Weixin Song, Colum M. O'Leary, Peter D. Nellist

University of Oxford, UK

Challenges in atomic-resolution imaging of battery materials include the difficulty in identifying light elements, such as Li and O, and electron beam-induced damage of the specimens. Electron ptychography in the scanning transmission electron microscope (STEM) is a method to reconstruct the phase information from the complex specimen exit wave function1, and when used in combination with annular dark-field (ADF) imaging, is sensitive to both heavy and light elements. Although annular bright-field (ABF) imaging can simultaneously visualize both light and heavy elements, ABF is not tolerant to residual aberrations and sample mis- tilting. Unlike ADF or ABF imaging where only a fraction of the scattered electrons are collected over a particular angular range, ptychographic phase reconstruction retrieves all the scattered electrons in the bright-field disk and is highly dose efficient2, 3. This high dose efficiency enables ptychographic phase reconstruction with high signal-to-noise ratios using beam currents below 1 pA, hence minimizing the damage induced by the electron beam. Furthermore, post-acquisition correction of residual aberrations reduces sample exposure to the beam, thus further reducing the beam damage.

Electron ptychography relies on the use of direct electron detectors that have a high detection efficiency to record two-dimensional (2D) diffraction patterns at each probe position
in a 2D raster scan, resulting in a 4D dataset. The dataset contains scattering information generated by the electron-specimen interaction and the ptychographic phase image is sensitive to both heavy and light elements. In addition, three-dimensional information can be obtained via ptychographic optical sectioning, where the ptychographic phase is reconstructed at a series of depths within the sample. For the characterization of battery materials, the combination of ptychographic phase reconstruction and ADF imaging can be used to identify the location of both heavy transition metals and light Li and O atoms in the projection. The ptychographic phase image enables the measurement of bond length. Any change of the bonds can demonstrate the local structural information of materials in electrochemical reaction, aiding the understanding of material properties and development of new materials.

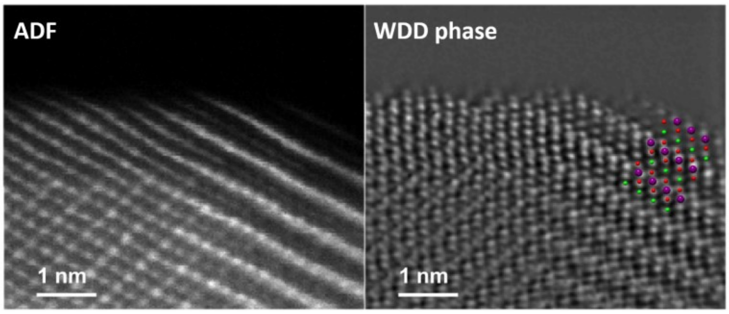

Figure 1 ADF and WDD phase image of Li-rich NMC. Inset: purple: TM; red: O; green: Li;

Lithium-rich $Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$ (NMC) is a high-energy cathode material because of the high specific capacity and voltage, resulting from the redox reaction of both transition metals (TMs) and oxygen ions. The complicated mechanisms have not been well understood. The lack of local structural information during redox hinders the further exploration. Here, we use electron ptychography and simultaneous ADF imaging to unambiguously identify Li, O and TM atoms in the structure. Figure 1 shows the ADF image and ptychographic phase reconstruction of pristine Li-rich NMC. The ptychographic reconstruction was performed using the Wigner distribution deconvolution (WDD) method. The polycrystalline Li-rich NMC presents multi lattice planes in the ADF projection and the none-on-zone planes of the edge reduce the resolution. In contrast, the WDD phase image shows robustness to the none-on-zone planes and enables the visualization of the atomic-resolution structure along $[010]_{C2/m}$ zone axis.

References

1.Nellist, P. D., et al., *Nature* **1995,** *374* (6523), 630.
2.Pennycook, T. J., et al., *Ultramicroscopy* **2015,** *151*, 160.
3.Yang, H., et al., *Ultramicroscopy* **2015,** *151*, 232.