

4D-STEM Mapping of Nanoscale Structural Ordering in Cathode Materials

Wenxiang Chen¹, Xun Zhan¹, Renliang Yuan¹, Saran Pidaparthy¹, Zhichu Tang¹, Jian-Min Zuo^{1*} and Qian Chen^{1*}

¹ Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign.

* Corresponding author: jianzuo@illinois.edu; qchen20@illinois.edu

Scanning transmission electron microscopy (STEM) has found great opportunities in studying transformation heterogeneity at the nanoscale in energy storage materials, such as the chemical phase separation [1, 2], cation ordering [3], and internal structures in electrode particles [4]. For example, our previous studies show that reduced particle size (< 100 nm) can effectively suppress the compositional heterogeneity in cathode particles during multivalent ion insertion [5]. Selected-area electron diffraction was employed to unravel the solid-solution phase formed in the cathode nanoparticles during phase transformation. Energy dispersive spectroscopy was used to visualize the composition non-uniformity in the cathode materials after electrochemical ion insertion, which is dependent on the particle size.

Here, we build upon this earlier effort of ours to further apply scanning electron nanodiffraction, also known as four-dimensional (4D)-STEM, to study transformation heterogeneity in cathode nanoparticles (Fig. 1). While our previous studies focus on the composition non-uniformity in the cathode materials, in this work we study the structural heterogeneity, exemplified by the phase orientation and strain, in cathode nanoparticles. To map phase orientations in a transformation system, the conventional methods of template matching and correlation mapping [6] have limitations, as they are either designed for a single-phase system or consider multiple factors beyond phase orientation. To solve this problem, we define a parameter of “tetragonality” to describe the local distortion on the cathode structure induced by ion insertion (Fig. 2a). Based on a fitting and segregating method, the “tetragonality” successfully distinguish the different phase orientations involved in the cathode nanoparticle transformation (Fig. 2b,c), clearly identifying each orientation domain, the group-subgroup relationship in the transition, and the domain morphology at various electrochemical conditions [7].

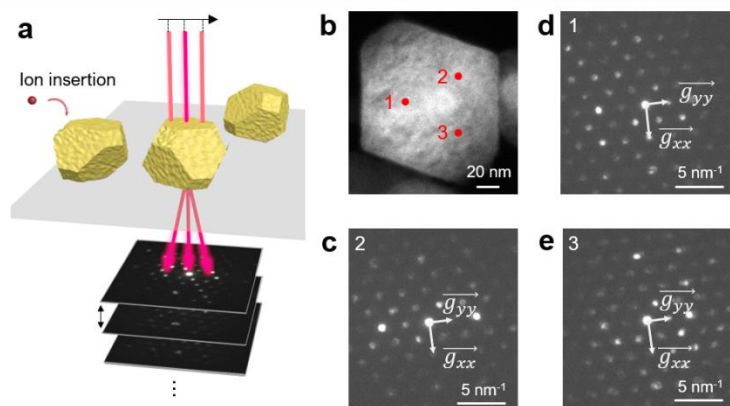


Figure 1. (a) A schematic showing 4D-STEM conducted on the cathode nanoparticles. (b) HAADF image of a cathode nanoparticle after electrochemical ion insertion and (c–e) three representative diffraction patterns collected by 4D-STEM on the cathode nanoparticle.

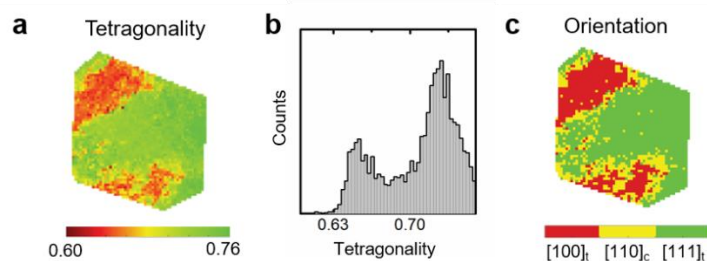


Figure 2. (a) The intensity map of “tetragonality” calculated from each diffraction pattern collected on the cathode NP shown in Fig. 1. (b) The histogram of “tetragonality” derived from (a). (c) The phase orientation map determined from the intensity map of “tetragonality”. “t” and “c” stand for tetragonal phase and cubic phase, respectively.

References:

- [1] G Brunetti et al., *Chem Mater* **23** (2011), p. 4515.
- [2] M Gu et al., *ACS Nano* **7** (2013), p. 760.
- [3] M Sathiya et al., *Nat Mater* **14** (2015), p. 230.
- [4] E Hu et al., *Nat Energy* **3** (2018), p. 690.
- [5] W Chen et al., *Nano Lett* **19** (2019), p. 4712.
- [6] J Zuo et al., *Microsc* **71** (2022), p. i116.
- [7] This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award no. DE-SC0022035.