

Revealing Near-Surface to Interior Redox upon Lithiation in Conversion Electrode Materials Using Electron Microscopy

Kai He¹, Huolin L. Xin¹, Jing Li^{1,2}, Eric A. Stach¹, and Dong Su^{1,2}.

¹. Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, USA

². Department of Materials Science and Engineering, Stony Brook University, New York, USA.

Lithium-ion batteries and supercapacitors both rely on electrochemical redox processes, although different mechanisms determine their relative energy and power densities [1]. For nanostructured electrodes of lithium-ion batteries, the capacity contains contributions from redox reactions that occur in both the interior (I) and near-surface (NS) regions. It is believed that the interior redox reactions contribute more to the overall battery capacity, but these take a longer time to be activated. In contrast, redox reactions in the near-surface reaction may exhibit a supercapacitor-like behavior (*i.e.* a high power density) because of the short transport paths for ions and electrons. Thus, an understanding of the kinetics of the transition from NS-redox to I-redox is critical to determining the rate capability of a lithium ion battery.

In this work, we performed TEM experiments using two setups: (I) TEM “grid-in-a-coin-cell” using liquid electrolyte, and (II) *in situ* lithiation using Li₂O solid electrolyte. The *in situ* measurements and tomography were performed on a JEOL 2100F TEM operated at 200 kV. The high-resolution imaging and analytical EELS were conducted on a Hitachi HD2700C STEM operated at 200 kV and equipped with a probe aberration corrector. Using combined electron microscopy approaches (*in situ* TEM/STEM, diffraction, tomography and STEM-EELS(Fig.1)), we observe the heterogeneous lithiation pathways that occur in NiO electrodes in real time (Fig.2). We find that the near-surface electroactive (Ni²⁺→Ni⁰) sites saturated very quickly, and then encounter unexpected difficulty in propagating the phase transition into the electrode (referred to as a “shrinking-core” mode). However, the interior capacity for Ni²⁺→Ni⁰ can be accessed efficiently following the nucleation of lithiation “fingers” which propagate into the sample bulk, but only after a certain incubation time. The reaction timescale and patterns we discovered from *in situ* TEM correlate with the ultimate rate performance of large-format batteries and are further supported by *ex situ* TEM and X-ray spectroscopies. We believe such heterogeneous transition mechanisms from NS-redox to I-redox may be generic and transferrable to a large class of conversion nano-electrode materials [2].

References:

[1] P Simon, Y Gogotsi, B Dunn, *Science* **343**, (2014), p1210-1211

[2] K He *et al*, Nano Letters, (2015) DOI: 10.1021/nl5049884

[3] The TEM work was carried out at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, under Contract No. DE-AC02- 98CH10886 and DE-SC-00112704. We acknowledge the collaborations from Kejie Zhao and Ju Li(MIT), Xiqian Yu and Xiaoqing Yang(Brookhaven National Lab) Dennis Nordlund and Tsu-Chien Weng (SLAC National Accelerator Lab) Yi Jiang(Cornell U), Christopher A. Cadigan and Ryan M. Richards(Colorado School of Mines) Marca M. Doeff and Feng Lin(Lawrence Berkeley National Laboratory)

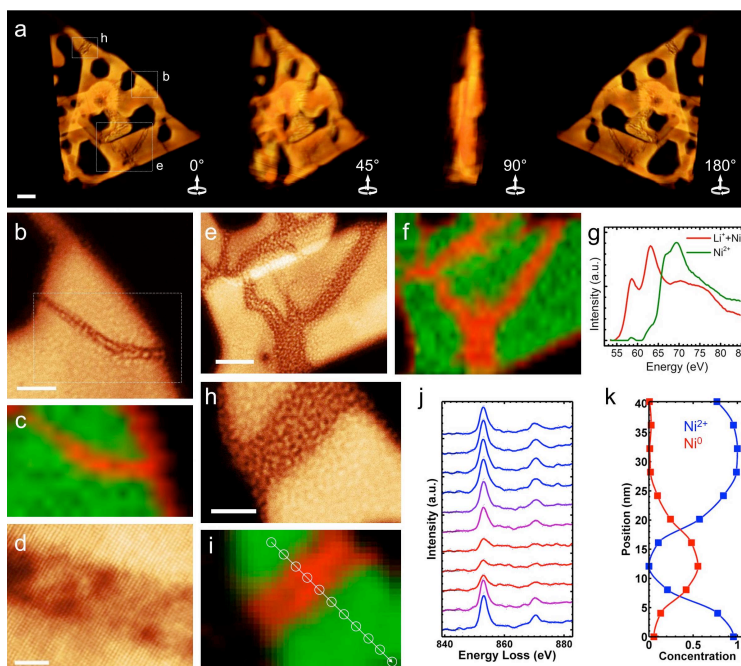


Figure 1. Tomography and EELS mapping of lithiated NiO fingers. (a) A series of reconstructed 3D tomograms from an in situ lithiated NiO nanosheet. (b), (e), and (h) are zoom-in ADF-STEM images corresponding to the labeled regions in (a). (c) and (f) show EELS mapping of Ni^{2+} (green) and $\text{Li}^+ + \text{Ni}^0$ (red) for areas in (b) and (e) using the low-loss spectra components shown in (g). (d) Atomically-resolved STEM image showing a crack region coherently bounded with un lithiated NiO in (b). (i) EELS charge mapping of Ni^{2+} (green) and Ni^0 (red) for the area in (h), a series of EELS spectra and $\text{Ni}^{2+/0}$ concentration profiles along the arrow are shown in (j) and (k), respectively. Scale bars, 20 nm (a), 10 nm (b), 2 nm (d), 20 nm (e), 10 nm (h).

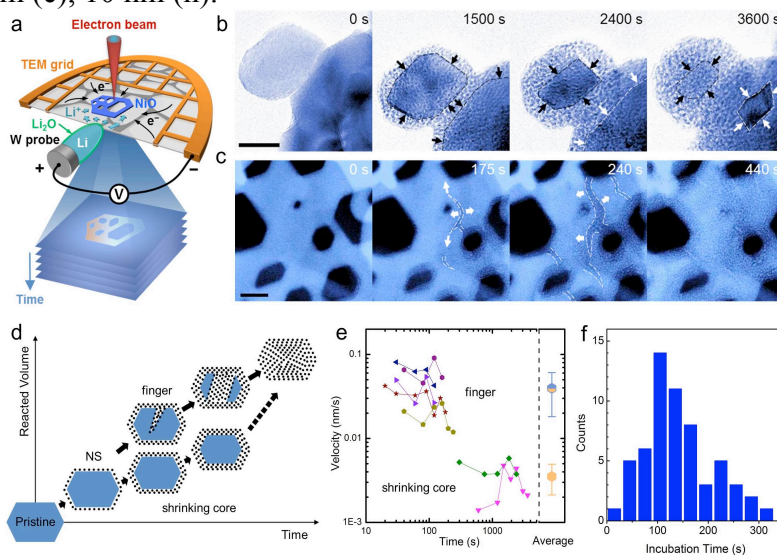


Figure 2. Structural evolution during in situ lithiation of NiO nanosheets. (a) Schematic illustration of in situ setup. Time-sequenced S/TEM snapshots (b) shrinking-core mode, and (c) finger mode. (d) Schematic cartoon showing heterogeneous pathways. (e) The velocity of reaction front propagation. (f) Histogram showing statistics of incubation time. Scale bars, 20 nm.