

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

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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

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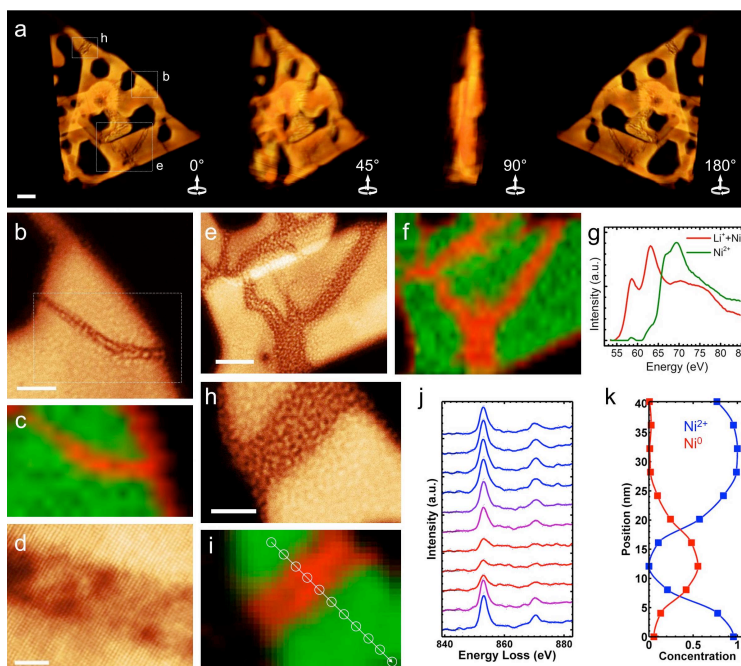


Figure 1. Tomography and EELS mapping of lithiated NiO fingers. (a) A series of reconstructed 3D tomograms from an in situ lithiated NiO nanosheet. (b), (e), and (h) are zoom-in ADF-STEM images corresponding to the labeled regions in (a). (c) and (f) show EELS mapping of Ni^{2+} (green) and $\text{Li}^{+}+\text{Ni}^0$ (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).

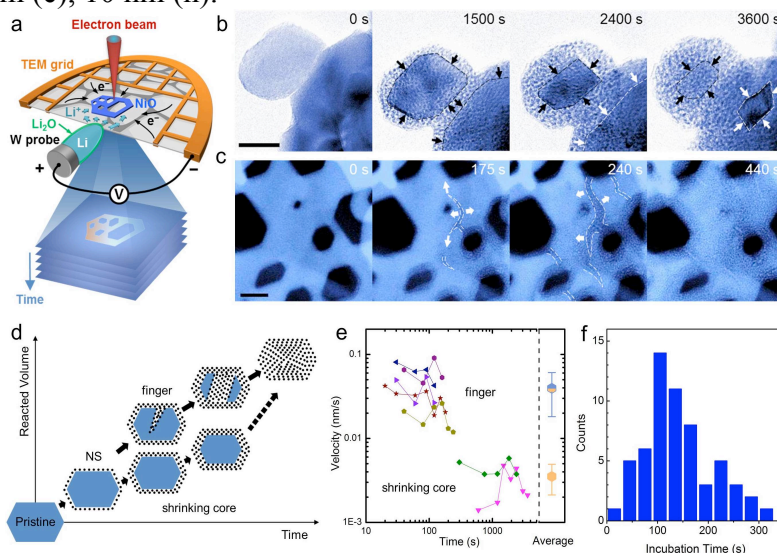


Figure 2. Structural evolution during in situ lithiation of NiO nanosheets. (a) Schematic illustration of in situ setup. Time-sequenced S/TEM snapshots (b) shrinking-core mode, and (c) finger mode. (d) Schematic cartoon showing heterogeneous pathways. (e) The velocity of reaction front propagation. (f)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