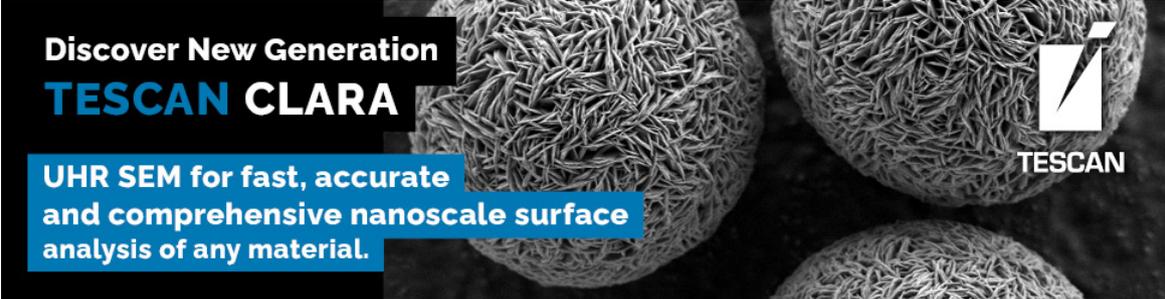


Correlative Mapping of Electrolyte-Dependent Microstructural Development in Cathode Materials

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Correlative Mapping of Electrolyte-Dependent Microstructural Development in Cathode Materials

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Scanning transmission electron microscopy (STEM) has found great potential in studying transformation heterogeneity at the nanoscale in energy storage materials, such as the chemical phase separation [1, 2], cation ordering [3], and defects such as planar gliding [4] and large pores [5] within electrode particles. For example, our previous studies show that reduced particle size (< 100 nm) can suppress the compositional heterogeneity in cathode particles during multivalent ion insertion [6]. Our correlative imaging method based on four-dimensional scanning transmission electron microscopy (4D-STEM) and electron energy loss spectroscopy (EELS) revealed for the first time the existence and evolution of transformation-induced “oriented phase domains” in cathodes during electrochemical ion insertion [7]. The domains are mapped and quantified by colocalized chemical composition and phase orientation at 2 nm resolution equipped with a novel data-mining approach, which leads to a ten-fold improvement in spatial resolution over previous reports [7].

Here, we build upon this earlier effort of ours to further apply correlative mapping to study the transformation heterogeneity in cathode nanoparticles in different electrolytes. While previous studies focus on the impacts of electrolytes on the solid-electrolyte interphases, in this work we study the role of electroactive species on the phase transformation in the cathode materials. For the comparison study, we choose two different electrolytes, which contain distinctive electroactive species with either strong ionic interaction or weak ionic interaction between the cation and the anion. Commercialized cathode nanoparticles (NPs) are selected as the model cathode system (Fig. 1). The transition between diffusion limitation and solid solutions regulated by the choices of electroactive species is observed in cathode NPs (Fig. 2) as characterized by an unconventional method of EELS mapping at 2 nm spatial resolution, which is difficult to achieve by X-ray microscopy [8]. The local accumulation of ions at the sub-particle surfaces causes significant lattice rotation and domain formation as revealed by 4D-STEM mapping. The experimentally observed phase morphologies enable the quantification of the effective ion migration barriers in the cathodes, which are shown to be regulated by electroactive species. Our results unveil the direct impact of electroactive species on the ion diffusion in the cathode materials, which rationally guide the design of new electrolytes with high electrochemical performance in energy storage systems [9].

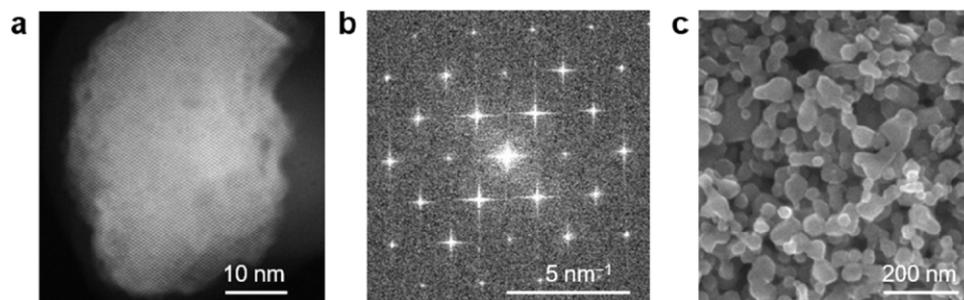


Fig. 1. (a) A scanning transmission electron microscopy (STEM) image of a pristine cathode nanoparticle (NP) (left) and the corresponding fast Fourier transform pattern (right). (b) An SEM image of the pristine cathode NPs used as the cathode materials.

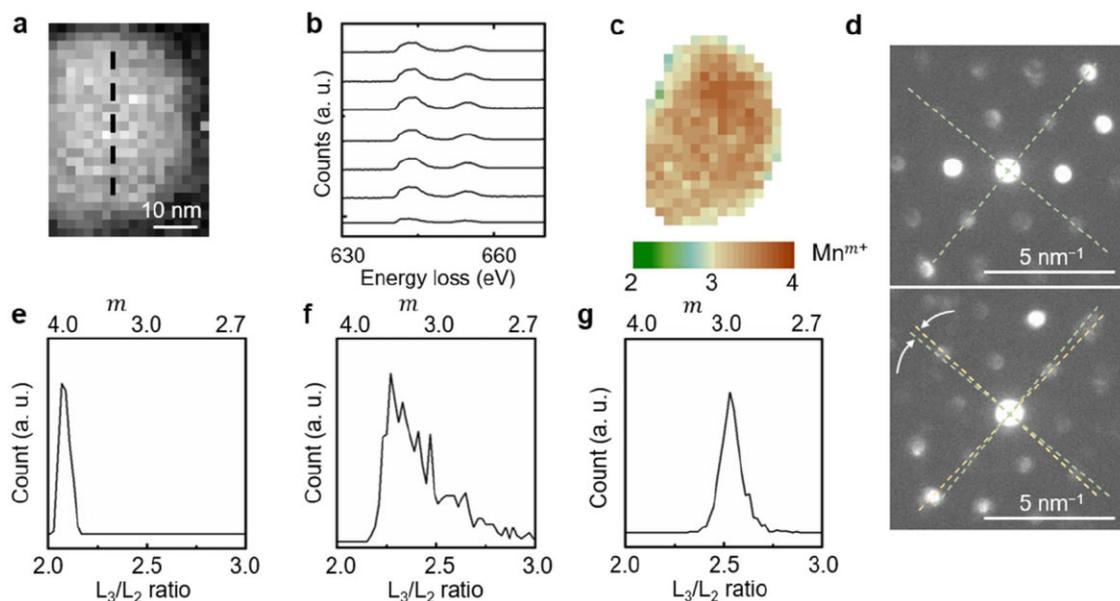


Fig. 2. (a) Virtual annular dark field image of a cathode NP at the end of discharge in the electrolyte with strong ionic interaction. (b) The representative electron energy loss spectra of Mn $L_{2,3}$ edges collected in the scanning mode along the dashed line on the cathode NP in (a). (c) The Mn^{m+} oxidation state (m) maps for the cathode NP in (a) measured based on Mn L_3/L_2 peak intensity ratio. (d) Diffraction patterns collected on a cathode NP at the end of discharge by 4D-STEM show a rotation of the local lattice structures in the cathode NP. (e–g) Histograms of the Mn L_3/L_2 peak intensity ratios and Mn^{m+} oxidation state (m) for a pristine cathode NP before discharge (e), a cathode NP after discharge in the electrolyte with strong ionic interaction (f), and a cathode NP after discharge in the electrolyte with weak ionic interaction (g).

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