

Nanoscale Vibrational Spectroscopy to Probe Li Motion at Individual Interfaces in Battery Materials

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The growing incorporation of electric vehicles and portable smart devices in our lives has placed higher requirements on the safety, performance, and longevity of batteries [1]. Facile ionic transport is a primary criterion to design future battery materials and configurations. However, interfacial ion transport, including both across interfaces between different battery components, e.g., electrode-electrolyte interfaces, and across grain boundaries within single components, e.g., in polycrystalline cathodes or solid electrolytes, is often sluggish. The relevant origin is still unknown largely because ion transport behavior in solids is correlated to local atomic arrangements, and a technique that can probe both atomic structure and ion transport behavior is still missing. Amongst properties of the migrating species that affect their transport, the low energy optical phonon frequency correlates strongly with the activation energy for ion transport [2]. Scanning transmission electron microscopy (STEM) has been widely used to probe atomic structure in all classes of materials. Recently, advances in monochromation of electron sources has enabled nanoscale vibrational spectroscopy to be performed in a STEM via electron energy loss spectroscopy (EELS). Thus, in monochromated STEM EELS we have a technique that can probe atomic structure and ion transport behavior simultaneously with better than nanometer spatial resolution. The technique has already demonstrated its efficacy towards investigating local compositional variation in the core-loss regime and changes in bonding arrangements due to compositional variation in the vibrational-loss regime, along with atomic resolution imaging across individual nanoscale interfaces [3,4]. However, it has not yet been used to characterize interfaces in battery materials, not to mention to correlate vibrational modes with ion transport behavior using electron microscopy. In this study, we use atomic scale STEM and monochromated EELS to investigate the correlation between composition, chemical bonding, atomic structure and vibrational modes in LiCoO_2 , a typical lithium ion cathode material, with a focus of exploring the potential of utilizing vibrational STEM EELS to probe local ion transport behavior.

Polycrystalline LiCoO_2 specimens were prepared for STEM EELS analysis by mechanical polishing and ion milling. Core-loss and vibrational-loss STEM EELS was performed on a Nion UltraSTEM100 monochromated, aberration-corrected STEM, operated at 60 kV. The probe convergence and spectrometer collection semi-angles were 35 and 25 mrad, respectively. Dispersions of 0.4 and 100 meV/channel were used to record all vibrational-loss and core-loss spectra, respectively.

Fig. 1a shows an atomic resolution high-angle annular dark field image of LiCoO_2 tilted into the [110] zone axis orientation, with a structure model showing the atomic positions of all elements overlaid on the image [5]. Fig. 1b shows a monochromated HAADF image of the grain boundary of interest. Grain 2 is tilted into the [110] zone axis before all STEM EELS acquisitions. Preliminary core-loss measurements (Fig. 1c) show that the relative Li to Co concentration drops by 35% at the grain boundary. Correlative vibrational-loss measurements (Fig. 2a) show a difference in the shape of the spectrum between 35 and 65 meV at the grain boundary. An aloof beam vibrational energy-loss spectrum (Fig. 2b) was acquired to remove the delocalized contribution to the transmission vibrational

spectra. The aloof spectrum consists of an out-of-plane and an in-plane hyperbolic phonon polariton, and a surface phonon polariton. After removing these polaritonic features, the residual non-alooof component consists of bulk features and Brillouin zone boundary phonons because of employing a 35 mrad convergence semi-angle [6]. The non-alooof component between 40 and 60 meV shows a clear shape difference in the Boundary spectrum relative to that from the grain interiors. Density functional theory (DFT) based phonon density of states suggest that this signal is associated with Li atom motion. Further experimental results and corresponding DFT and inelastic electron scattering simulations will be presented [7].

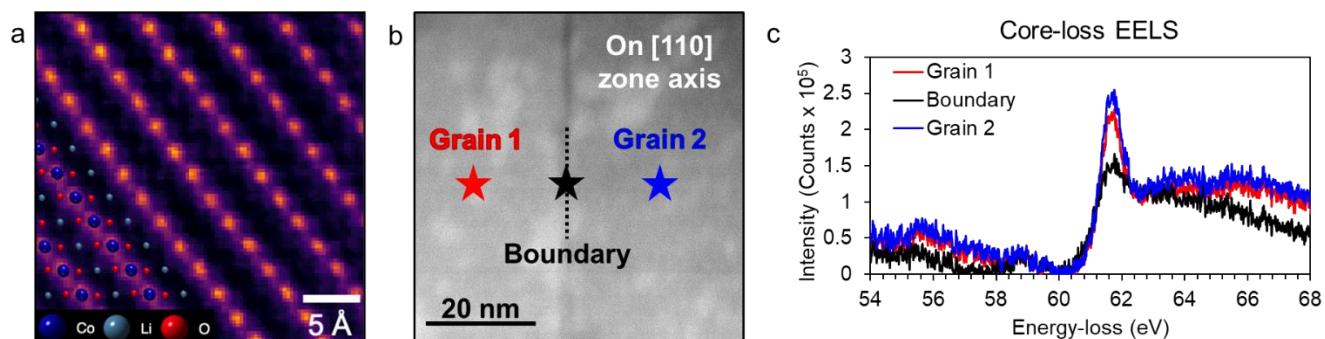


Figure 1. a) Atomic resolution HAADF image of LiCoO₂ in [110] zone axis orientation with an overlaid structure model [5]. b) Monochromated HAADF image of a grain boundary in a polycrystalline LiCoO₂ specimen showing probe positions for EELS acquisitions in Figures 1c and 2a. b) Background-subtracted core-loss EELS showing a drop in the Li K-edge relative to the Co M2,3-edge at the grain boundary.

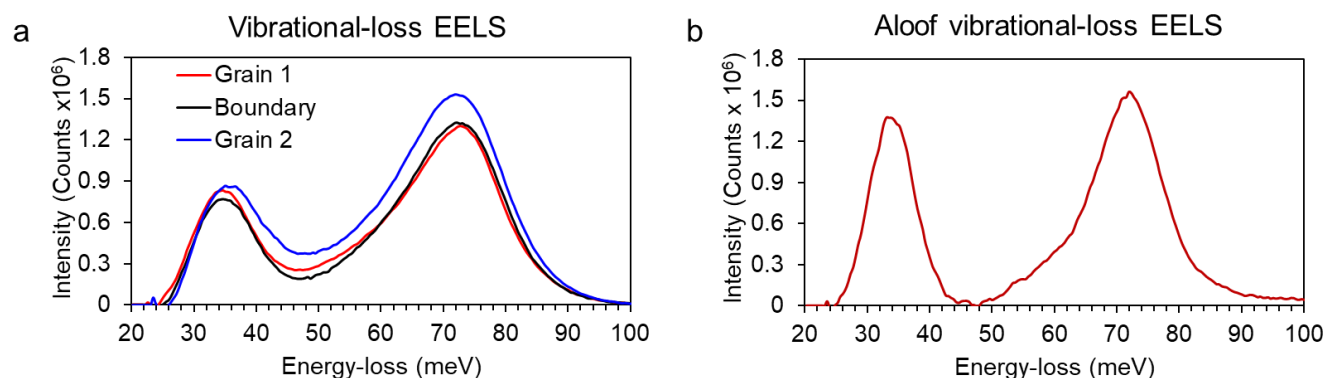


Figure 2. a) Background subtracted transmission vibrational EELS measurements from the grain interiors and the boundary. b) Aloof-beam vibrational EELS from LiCoO₂ showing the contribution from polaritonic features.

References:

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