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Imaging surface morphology, chemistry and conductivity, and local spectroscopy of $\text{LiNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{4/3}\text{O}_4$ crystalline facets using XRF/TEY implemented scanning transmission X-ray microscopy

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Scanning transmission X-ray microscopy (STXM) using the X-ray fluorescence mode has been employed to elucidate the chemical structures at Ni, Fe, Mn and O sites from (111) and (100) facets of micron-sized $\text{LiNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{4/3}\text{O}_4$ energy material particles. Furthermore, STXM imaging using the electron yield mode has mapped out the surface conductivity of the crystalline particles. This study presents a novel approach that visualizes local element segregation, chemistry and conductivity variation among different crystal facets, which will assist further tailoring the morphology and surface structure of this high voltage spinel lithium ion battery cathode material.

Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) is an attractive cathode material for lithium ion battery (LIB) because of its high energy and power density (4.7 V charge-discharge plateau and the three dimensional lithium diffusion paths^{1,2}), low toxicity and low cost. However, to apply it in electric-drive vehicles, issues involving the stability of electrode and electrolyte at high voltage, and their dependence on the crystalline structural ordering, doping/substitution, and impurity need to be better understood³⁻⁷. Our previous X-ray absorption near edge structure (XANES) study shows surface and bulk chemical structure difference and its evolution as a function of the state of charge². This difference was interpreted as a result of the side reaction under high voltage for LNMO, especially at the Ni site with electrolyte². Mn dissolution possibly associated with this side reaction is a fatal effect in a full battery cell with graphite as the anode^{5,8}. Such side reactions must be related to LNMO surface structures, including cation ordering, ratio of cations, and crystallographic facets and shapes. For instance, significant improvement of the electrode-electrolyte stability was observed on the (111) facet, which was attributed to the formation of a stable passivation film on this facet⁷. It is understandable that surface energy associated with specific facet will impact the kinetics and thermodynamics of heterogeneous reaction at the electrode-electrolyte interface⁹. Morphology engineering to obtain preferred (111) facet dominated LNMO has been investigated and the performance

has been greatly improved^{10, 11}. LNMO with different crystalline morphologies (nanoparticle, octahedral and truncated octahedral) have been synthesized and various characterization techniques (such as XRD, TEM, Raman, and hard X-ray XANES) have been applied to evaluate the structure difference among them. By combining comprehensive electrochemistry of LNMO with different morphologies, it has shown that increasing the ratio of (100) over (111) facet results in a better rate and cycling performance¹¹. However, the difference in electronic structure and chemistry (the root cause of the resulted electrochemistry) between phase pure LNMO crystalline facets was not investigated and thus less understood. Furthermore, surface coating has been demonstrated as an effective way to improve the stability of LNMO when being operated at high voltage⁸. To progress the rational design of LNMO in facet tailoring and surface modification, advanced characterization tools such as scanning transmission X-ray microscope (STXM) need to be utilized. Hard X-ray based Transmission X-ray Microscopy (TXM) has deeper penetration depth than soft X-ray based STXM. Hard X-ray TXM can explore phase and chemistry transformation at transition metal site from a specially designed electrochemical cell¹². However, the chemical and electronic structure of the surface, subsurface and interface in the battery materials cannot be easily explored by TXM. Additionally, the light elements such as C, F and O, which are part of solid electrolyte interface, cannot be studied by hard X-ray based TXM and can only be accessed by soft X-ray based STXM. STXM has been successfully applied to chemical imaging of various nanomaterials¹³, as well as revealing the correlation of electrochemical performance with the chemical bonding in the hybrid electrode active materials¹⁴ and phase transformation within a porous electrode¹⁵. However, the conventional STXM in the soft X-ray energy range requires thin sections or fine particles of the sample with thickness/size of tens to hundreds of nanometers, which appears to be substantially challenging for large LIB crystalline materials of a few micrometer size. To overcome this issue, imaging through energy dispersive X-ray fluorescence (XRF) and total electron yield (TEY) has been explored in STXM for thick LIB crystalline materials in this work. XRF-STXM using silicon drift detector (SDD) had been developed and applied to a study of environmental biofilm samples¹⁶ to obtain elemental mapping and chemical speciation with significantly enhanced sensitivity for low concentration elements. In this letter, the surface of micro-sized Fe doped LNMO particles ($\text{LiNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{4/3}\text{O}_4$) was measured by XRF-STXM in order to understand the excellent electrochemical performance along with significantly improved thermal stability¹⁷. This work will not only deepen our understanding of the correlation among morphology, surface element distribution and chemistry, and surface conductivity in this promising, high energy density, high thermal runaway resistant material, particularly on the role of Mn^{3+} and facet in conductivity and rate performance¹⁸, but will also lay a ground for applying the XRF/TEY-STXM to other battery electrode materials, especially for modified surface before or after battery operation. This work on a pristine electrode material will provide an accurate understanding without the

interference from other battery chemical components and lay a solid ground for future study of the cycled LNMO, as the performance of the electrode is largely dependent on the pristine material. In addition, it gained valuable experience for future in-situ STXM of mimic lithium ion battery which has been under development at CLS.

Detailed studies on the structure characterization, electrochemical performance and thermal stability of this Fe doped LNMO, can be found in a previous publication¹⁷. The STXM measurement of pristine $\text{LiNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{4/3}\text{O}_4$ was performed at the SM beamline of Canadian Light Source (CLS) in a vacuum chamber at $\sim 10^{-3}$ Torr. The powder sample was first dispersed in methanol and then casted onto a 20 nm Au coated Si_3N_4 window as the specimen. The monochromatic X-ray beam is focused by a Fresnel zone plate lens to a ~ 30 nm spot on the sample. The sample is raster-step-scanned with synchronized detection of XRF yield (sampling depth ~ 100 nm) using an Amptek^{TM} X123 silicon drift detector (SDD), and surface sensitive total electron yield (TEY, sensitive to the top ~ 5 -10 nm) by recording the sample current. Empty sample region was simultaneously measured in the transmission mode to provide incident X-ray flux profile for normalization. Chemical imaging and XANES spectra are obtained using image sequence (stack) scans over a range of photon energies across interested element absorption edges. STXM data was analysed by aXis2000 (<http://unicorn.mcmaster.ca/aXis2000.html>).

Ni, Mn, Fe $L\alpha$ and O $K\alpha$ XRF emissions were used to record image stacks at respective element edges. This energy-selected X-ray emission can eliminate the self-absorption effect which is common in FY XANES experiment². Figure 1 shows elemental mapping of micron-sized $\text{LiNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{4/3}\text{O}_4$ by averaging the XRF imaging stack at each element edge. First of all, it is visible that primary particles with size of several micrometres are aggregated into secondary particles in the dimensions of larger than 10 micrometres. For this size/thickness conventional transmission based STXM will not

work since soft X-ray will be completely attenuated, therefore impossible to get such nice elemental mapping. Secondly, the morphology of the primary particles has been well resolved and identical in all XRF maps, which suggests uniform distribution of the elements in the measured sample region. However, a close examination reveals that Ni and Fe maps show better defined crystallographic facets than those of O and Mn. The particles exhibit a typical truncated octahedral shape which is due to its spinel structure¹¹. Two sets of (111) (hexagon shape) and (100) (quadrangle shape) facets are identified in Ni and Fe map, labelled in Fig. 1a and c. Clearly, Ni and Fe spatial distribution varies among facets and edges more substantially than that of Mn and O does. This results in better facet contrast in Ni and Fe maps. In addition, there are bright spots with dimensions around a few hundred nm enriched on edges between facets in Fe and Ni maps which correspond to the Ni and Fe segregation in those regions. Further visualization of elemental association and segregation was achieved by rescaled color-coded composite maps of different combinations of individual elements as being displayed in Fig.1 (f) to (i). Fig. 1f overlapped Ni/Mn/Fe and confirmed Ni/Fe segregations into small particles (an example region was pointed by arrow 1) on facet edges while distribution of Mn is more homogeneous. Ni/Mn correlation was visualized in Fig. 1g and suggests the particles with more Ni/Fe segregation have lower Mn content. Interestingly, this color-coded map also displays regions with Mn rich as pointed by arrow 2 in Fig. 1g. The Ni/Fe association mapping is shown in Fig. 1h which reconfirmed the high association between Ni and Fe, but regions with Fe rich can also be founded as labeled by arrow 3. Finally the Mn/O association is very uniform across all mapped facets and particles, as shown in Fig. 1i. It is noted that elements association varies between particles and facets even with same crystallographic orientation.

Fig. 1 Morphology and element distribution for Ni (a), Mn (b), Fe (c) and O (d) of $\text{LiNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{4/3}\text{O}_4$ by XRF-STXM at respective element edges. Two sets of (111) and (100) facets are labelled in (a) and (c). (e) illustrates the two facets in the truncated octahedral spinel crystal. Rescaled color-coded composite maps of the Ni, Mn, Fe in (f), Ni, Mn in (g), Ni, Fe in (h), and O, Mn in (i) by overlapping individual elemental maps displayed in (a) to (d). The color codes were displayed in each figure.

Fig. 2 Ni (a), Mn (b), Fe (c) L_3 -edge and O (d) K-edge XANES of adjacent $\text{LiNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{4/3}\text{O}_4$ (111) and (100) facet (the right upper set of facets labelled in Fig. 1(a)) extracted from XRF-STXM stacks. Fig 2(b) inset displays the Mn L-edge XANES from phase pure ordered and disordered LNMO powders.

The chemistry in interesting regions has then been studied by XANES extracted from XRF-STXM image stacks. This is a very important merit of STXM which can interrogate samples at fine spatial scale for chemistry speciation. We first examine the chemistry difference between different crystallographic facets in Fig. 2. The roles of facets on side reaction and lithium diffusion have been extensively studied and been proved to be crucial to the battery life and rate performance. It is generally accepted that the (111) facet is more stable, but the (100) facet promotes higher Li diffusion^{7,11}. Therefore, experimental study of the chemistry difference between those facets, especially within single particles, will help optimize further facet tailoring and engineering. From Fig. 1 and 2 we know the elemental composition between adjacent facet (111) and (110) is very close (i.e. the right upper set of facets labelled in Fig. 1(a)), so the chemistry study will be dominated by crystalline orientation effect. Fig. 2a to c are Ni, Mn and Fe L_3 edge XANES, respectively, which arises from the electronic transitions from the metal 2p level to its mostly unoccupied 3d states, therefore it is sensitive to oxidation state, covalence as well as spin states¹⁷. The overlapped Ni L_3 XANES between (111) and (100) suggests the chemistry at Ni sites is same between those two selected facets. The spectrum features the low spin Ni^{2+} with electronic configuration of $t_{2g}^6 e_g^2$. Fig. 2b displays Mn L_3 edge XANES of those two facets. Similar to the Ni case, Mn L_3 edge involves the electronic transitions from Mn $2p_{3/2}$ to Mn 3d states, and it is useful to study oxidation state, spin and covalence at Mn sites. Spectrum of facet (111) presents Mn^{4+} dominated features^{19, 20}, which agrees with theoretical expectation that Mn remains at Mn^{4+} in the pristine LNMO. However Mn XANES of facet (100) is different in terms of the enhanced feature at 642 eV, which is a spectroscopic evidence of Mn^{3+} ²¹. LNMO has two different Ni/Mn arrangements, i.e. the Ni/Mn ordered phase and disordered phase¹. It has been found that the Ni/Mn disorder is correlated with the formation of oxygen vacancies, denoted as $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-6}$.¹ In this case the Mn oxidation state will reduce to balance the charge lost in oxygen, which means an increase of Mn^{3+} . We collected Mn L-edge XANES from phase pure ordered and disordered LNMO, as shown in Fig. 2b, and did find the relative increase of the Mn^{3+} in the disordered LNMO. This could mean a relative increase of disordered on (100) facet. The current STXM results also agree with literature⁷ that the (111) facet has less Mn^{3+} . However, as we have shown in Fig. 1 same crystalline orientation (111) facets have dramatically different chemical composition, XRF-STXM with the ability to choose pure composition crystals to study their chemistry is a more reliable method to study facet dependent chemistry. Mn oxidation has been reported to affect electronic conductivity¹⁸ and this will be investigated by TEY-STXM in a following section. Fe oxidation and spin states from those two facets are explored by Fe L_3 edge XANES as shown in Fig. 2c.

The Fe spectra from two facets are similar to each other and characterize high-spin Fe^{3+} as being reported in our previous work¹⁷. The observed same spin state for Fe dopant from different facets may coincide with the excellent thermal stability as being reported. The capability of investigating spin state from well-defined facets by XRF-STXM in this work will help optimize facet engineering when doping is applied. Finally, difference between those two facets was studied by O K-edge XANES as shown in Fig. 2d to gain insights of electronic structure and chemistry from the perspective of oxygen site. The O K-edge XANES arises from the dipole transitions from O 1s to the unoccupied orbitals with dominant p character. Pre-edge peaks at 530 eV and 532 eV reflect hybridization of O 2p and metal (Ni, Fe and Mn) 3d orbitals, and the broad peaks from 534 to 552 eV are due to hybrid states of O 2p with metal 4sp characters. Generally, those two spectra, particularly at the pre-edge region, are similar to each other and resemble LNMO as reported in our previous publication in which the O K-edge XANES is dominated by Ni^{2+} and Mn^{4+} features. O $K\alpha$ fluorescence has slightly longer attenuation length than that of Mn $L\alpha$ fluorescence (http://henke.lbl.gov/optical_constants/atten2.html), which might account for the inconsistency on Mn oxidation derived by O K-edge and Mn L-edge XANES, even though we cannot exclude the possibility of surface reorganization effect. Furthermore, the difference between two spectra at the O 2p/metal 4sp hybridization region is obvious that facet (111) shows enhanced and broadened peaks. Cycled LNMO has shown similar spectroscopic changes which have been attributed to delithiation and/or solid electrolyte interface (SEI)² formation with the existence of Li_2CO_3 ²².

Finally, TEY-STXM image stacks at Mn L_3 edge was obtained by recording sample current when sample was raster scanned under specific photon energies. Fig. 3 left shows the TEY-STXM mapping which displays bright and dark regions along with the morphology contrast. The bright region corresponds to higher TEY yield comparing to that in the dark region. TEY is a direct measure of the X-ray absorption process which can be used to record XANES spectrum. Mn L_3 -edge XANES from those two regions can be used to compare the Mn concentration in those two regions. The absolute edge jump (the intensity difference before and after the absorption edge) in STXM mapping is proportional to the concentration under study²³. Apparently, as presented in the left figure inset, the smaller edge jump in the bright region confirms the relatively low concentration of Mn in this region. It is known that good sample conductivity is needed for TEY XANES measurement²⁴, thus the higher TEY yield in this mapping should be caused by a better electronic conductivity. Furthermore, the electronic structure and chemistry difference were evaluated by normalized Mn L_3 XANES shown in Fig. 3 right panel. The dark region shows higher ratio of 644 eV peak over 641 eV peak, which hints more Mn^{4+} in the low conduction region. In contrast, the higher conductivity region (bright region) apparently shows more Mn at lower oxidation state which enhances the peaks at lower photon energy. Though the morphology contrast in the TEY-STXM mapping is not as good as that by XRF-STXM, the shape of the centre dark region is close to a (111) facet and the bright regions are quite possible to be facet (100). As discussed above and in literature¹⁸, Mn with lower oxidation may contribute to higher electronic

conductivity and this is a first experimental evidence to correlate them.

Fig. 3 TEY-STXM imaging of pristine $\text{LiNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{4/3}\text{O}_4$ (left) and Mn XANES from high and low conductivity region (absolute intensity spectra in the left panel inset, and normalized spectra in the right panel).

XRF- and TEY-STXM have been applied to interrogate Fe doped LNMO to obtain correlation between morphology, elemental segregation, chemistry and conductivity (via indirect mapping) at 30 nm scale to elaborate our understanding of its excellent thermal stability and electrochemical performances from the structural perspective. The ability to explore all of those critical properties from a single pristine particle can avoid inconsistencies caused by sample synthesis and preparation, therefore provide a solid ground for abovementioned fundamental issues. Uniform elements distribution were confirmed though existence of small particles (~a few hundred nm) with relative high Ni/Fe concentration. It also showed that same crystalline orientation (111) has different elemental concentration. This highlights the importance and unique strength of microscopic study of facet-dependent chemistry. Higher portion of Mn^{3+} was found in facet (100) compared to that in facet (111) by both XRF- and TEY-STXM for the first time which hints more disordered LNMO at (100) facet. But interestingly, the two facets have very similar O, Ni and Fe chemistry and spin states. Since our previous paper¹⁷ has shown that the Fe spin state is critical in managing the thermal stability of this Fe doped LNMO and the electronic structure at those sites determines the electrochemistry, the similarity of the soft X-ray XANES between those two dominate facets reveals the micro structural identity of the observed improved thermal stability and good electrochemistry¹⁷. TEY-STXM can map out high on (100) facet and low TEY regions on (111) facet which might be related to conductivity. Mn with lower oxidation number associates with higher TEY, which might represent better conductivity. This coincides with the fact that a better rate performance in truncated octahedral LNMO particles was observed with increased portion of (100) facets over (111)¹¹. Knowledge obtained from this study shall find usage in guiding rational facet and doping engineering of LNMO. It should be emphasized that those techniques can be applied to studies of surface coating, SEI formation of electrode materials not limited to LNMO from in-situ or ex-situ of an electrochemical cell^{2, 14, 15} owing to the sensitivity in light elements and low concentration which is not accessible from hard X-ray microscopy¹².

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