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Near-edge X-ray refraction fine structure microscopy

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We demonstrate a method for obtaining increased spatial resolution and specificity in nanoscale chemical composition maps through the use of full refractive reference spectra in soft x-ray spectro-microscopy. Using soft x-ray ptychography, we measure both the absorption and refraction of x-rays through pristine reference materials as a function of photon energy and use these reference spectra as the basis for decomposing spatially resolved spectra from a heterogeneous sample, thereby quantifying the composition at high resolution. While conventional instruments are limited to absorption contrast, our novel refraction based method takes advantage of the strongly energy dependent scattering cross-section and can see nearly five-fold improved spatial resolution on resonance. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4975377]

Soft x-ray spectro-microscopy is a powerful analytical technique for quantitative chemical and morphological characterization of materials, which can probe electronic states of matter with high specificity and spatial resolution.1–8 It also offers the added advantage of higher material penetration and potentially less radiation damage than other spectro-microscopy techniques such as electron energy loss spectroscopy (EELS).9 In traditional scanning transmission x-ray microscopy (STXM), the sample is raster scanned through a focused x-ray beam and at each point the total transmitted intensity is measured as a function of photon energy in the vicinity of atomic resonances, which enables the extraction of spatially resolved near-edge x-ray absorption fine structure (NEXAFS) spectra. Although the material contrast may change dramatically with energy, following the energy dependence of the materials’ refractive indices, the achieved spatial resolution for STXM is essentially constant with the x-ray spot size. Alternatively, x-ray ptychography can provide spatial resolution significantly finer than the spot size through phase-retrieval based inversion of x-ray diffraction data, which can be recorded to a numerical aperture far larger than is technically feasible to manufacture in x-ray optics.10–15 Since the energy dependence of the coherent scattering cross-section is also dominated by the variation of a material’s refractive index near an atomic resonance, the scattered signal and hence the achieved spatial resolution as well as the chemical contrast can be dramatically enhanced.

X-ray ptychography is conceptually similar to STXM, except that a full diffraction pattern is measured at each sample scan position and the x-ray wavefield exiting the sample is subsequently reconstructed numerically by a phase retrieval algorithm. When the scan positions overlap sufficiently, there is a high data redundancy that makes phase retrieval through iterative reconstruction possible and yields the local complex transmission function, both absorption and phase shift, of the sample as well as the complex illumination function.10 Rather than the optical point spread function, ptychographic spatial resolution is instead limited primarily by the angular extent of the measurable diffraction pattern. This, in turn, depends upon the material refractive index, \( n = 1 - \delta + i\beta \) (with \( \beta \) related to absorption and \( \delta \) to dispersion) that is strongly energy dependent in the vicinity of atomic resonances. Of course, additional experimental factors, such as relative sample and probe positioning accuracy, can reduce the spatial resolution but they are straightforward to establish at the nanometer scale.

For a broad class of materials, the increased sensitivity to relative phase shift that ptychography brings can result in higher fidelity chemical composition maps and hence better quantification. Indeed, previous work has demonstrated chemical contrast in ptychographic imaging via both absorption and phase16 as well as measurements of the full refractive index of heterogeneous materials as a function of energy.13,15,17–19 These works, however, do not achieve quantitative chemical analysis of materials, which requires comparison with independently measured reference spectra that are used as the basis for expansion of mixed spectra.20,21 Here, we present a novel method of chemical mapping from ptychographic reference spectra, that is, measurements of \( \delta \) and \( \beta \) as a function of energy, which achieves higher spatial resolution and higher chemical specificity than conventional methods because of the availability of the full complex refractive index. Such spectra are measured for multiple pristine materials and used to map composition in a heterogeneous sample. We also quantify by numerical simulation how the ptychographic spatial resolution depends on energy.

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near an atomic resonance. The achieved spatial resolution presents a maximum at the energies that have the most negative phase shift relative to vacuum, or rather, the maximum phase difference relative to non-resonant material.

We choose pristine and partly delithiated nanoparticles of LiFePO₄ as a model system because it is widely studied as the cathode material in state-of-the art Li-ion batteries and it is known to undergo a two phase separation upon discharge and delithiation to FePO₄. The two chemical phases can be readily identified using soft x-rays by probing the Fe redox state, which is reduced by the presence of Li and results in a $2p^{3/2}$ transition shifted lower by 2 eV. The delithiation mechanism of LiFePO₄ has been the subject of numerous theoretical and experimental studies, and soft x-ray ptychography is particularly useful as a characterization tool for this material since monitoring the separation of phases in single crystals requires a spatial resolution below 10 nm and high chemical sensitivity. Reference spectra for pristine LiFePO₄ and FePO₄ were measured around the Fe L₂ and L₃ edges, with an energy step of 0.25 eV, at the Advanced Light Source (ALS) x-ray bending magnet beamline 5.3.2.1. Since measurement of the complex spectra is tied to the ptychographic imaging process, it requires measuring a three dimensional dataset by imaging the pure material at multiple energies and then extracting an average spectrum from a region of interest (ROI). The pristine standard samples are in the form of agglomerates of nanoplates with dimensions of 100 × 80 × 20 nm³. For brevity, images of only the LiFePO₄ sample are shown in Figure 1 at two energies: (a) pre-edge at 700 eV and (b) on the absorption resonance at 708 eV with resolutions of 14 and 9 nm, respectively, using Fourier Ring Correlation (FRC) with a half-bit threshold. Since the material scattering strength is nearly an order of magnitude higher on resonance, the diffraction pattern extends to larger angles and the image presents higher spatial resolution with the plate thickness resolved. Figure 2 shows a comparison of the calculated and measured refractive spectra obtained from the full set of images. The calculated spectra derive the real part of the refractive index from a Kramers-Kronig inversion of independently measured bulk NEXAFS spectra. All spectra were normalized by first subtracting the pre-edge data to minimize thickness effects and then scaling to unity optical density on the absorption resonance. As can be seen, the experimental and calculated data do follow the same general trend, but there is significant deviation in the phase component, with both additional fine structure and differences in relative peak heights being apparent. These differences are likely due to a combination of the improved sensitivity of ptychographic measurements, imperfect calculation of the phase via Kramers-Kronig inversion over a finite energy range, and subtle saturation effects in the spectra. Since calculated $\delta$ values are only numerical estimations based on $\beta$ obtained from experimental NEXAFS spectra, the experimental ptychographic spectra should be more accurate and detailed features not accessible through calculation are now

FIG. 1. Experimental ptychographic scattering contrast images of the pristine LiFePO₄ standard sample recorded at the pre-edge energy of 700eV (a) and on the absorption resonance of 708 eV (b). The image recorded on the absorption resonance shows higher resolution such that the individual particles with 20 nm thickness can be resolved (inset). (c) FRC curves for the images in (a) and (b). The data were split in half columnwise for the resolution analysis.
We define here the scattering contrast coefficient, \[ c^2 = \left( \frac{d^2 + b^2}{k^2} \right), \] which is related to the cross-section for coherent scattering and allows us to account for the full refractive contrast with a single real number. We note the similarity between this coherent scattering contrast function and the contrast function defined for resonant soft x-ray scattering (RSOXS). The scattering contrast spectra are shown in Figure 2 and present two well-defined peaks, at 708 eV and 710 eV, thus providing for quantitative chemical specificity.

To experimentally examine chemical composition mapping with refractive reference spectra, an agglomerate of partially discharged LiFePO\(_4\) (x \approx 0.5) was imaged. This agglomerate consists again of nano-plates electrochemically discharged to a 50% state of charge. Figures 3(a) and 3(b) show two ptychographic images of the agglomerate at 708 eV and 710 eV, respectively. The red and blue arrows point to regions rich in LiFePO\(_4\) and FePO\(_4\), respectively; note that as expected regions rich in LiFePO\(_4\) exhibit high (white) contrast at 708 eV and as the energy is increased to 710 eV, their contrast decreases sharply (the reverse is true for regions rich in FePO\(_4\)). Hence, using a ptychographic stack of images, measured at multiple energies, the energy dependent scattering contrast can be extracted. The individual complex valued images can be converted to a real number, \( \Psi \), which is proportional to the scattering contrast and has the same functional form as the optical density (\( 2\pi\beta t/\lambda \), traditionally used for chemical mapping)

\[
\Psi(\mathbf{x}) = \sqrt{\left[ -\ln \left( \frac{\psi(\mathbf{x})}{\psi_0} \right) \right]^2 + \text{Im} \left[ \ln (\psi(\mathbf{x})) \right]^2} = 2\pi\beta t(\mathbf{x}),
\] where \( \psi(\mathbf{x}) = \psi_0 e^{2\pi i (\beta x^2/\lambda)} \) is the complex valued x-ray wavefield exiting the sample, \( \psi_0 \) is the average value of the portion of the image unobstructed by the sample (i.e., the incident wavefield propagated through a distance of vacuum.

FIG. 2. Measured reference spectra for LiFePO\(_4\) (red, Fe\(^{2+}\)) and FePO\(_4\) (blue, Fe\(^{3+}\)). The ptychographic spectra (solid lines) show the same general trend as the conventional spectra (dashed lines) but exhibit significant differences in the phase component. Conventional absorption spectra are obtained by NEXAFS measurements while the conventional phase spectra are calculated via a Kramers-Kronig inversion of the absorption spectra. Bottom: scattering contrast spectra for the two components relative to vacuum (red and blue) and relative to each other (black dashed). The two well resolved peaks provide the chemical specificity required for quantitative chemical composition mapping.

FIG. 3. (a) and (b) Experimental scattering contrast images of partially discharged cathode agglomerate (50% state of charge) at two energies with peak contrast for the two components (708 for LiFePO\(_4\) and 710 for FePO\(_4\)). The arrows point to Lithium rich (red) and Lithium poor (blue) regions. (c) Chemical composition map of the agglomerate obtained through mapping the experimental total contrast spectra of the two components. (d) R-factor map of the linear fitting shown in (c).
equal to the sample thickness, assumed flat), $\lambda$ is the x-ray wavelength, and $r(\xi)$ is the unknown map of the material thickness. Following the method of Lerotic, thickness effects can be removed from the composition maps through a combination of principal component analysis and singular value decomposition.\textsuperscript{20,21} Figure 3(c) shows the chemical composition map obtained in this fashion. The R-factor distribution indicates very good agreement between the measured data and the fit to the reference spectra (supplementary material).

Since the exact solution for an arbitrary sample cannot be known, the use of a simulated structure makes it straightforward to visualize and quantify the energy dependence of resolution and contrast. To investigate the variation of resolution with energy, a series of simulations were carried out, with a three-component system resembling that of the LiFePO$_4$/FePO$_4$/50% mixed state. Figure 4 shows the reconstructed resolution as a function of energy along with a plot of the energy dependent scattering contrast. All reconstructions contained the same number of incident photons. It is interesting to note that the maximum image resolution occurs at an energy slightly below the total contrast peak and the resolution of the chemical map is similar while being nearly a factor of five higher than the off-resonance resolution. The peak falls at the energy of the most negative phase shift relative to vacuum, which yields the maximum phase contrast relative to the non-resonant material and points to phase contrast being a primary driver in ptychographic image resolution. The spatial resolution of the off-resonant images could be improved simply with increased x-ray exposure time (to compensate for weaker scattering contrast) but this result indicates that is not necessary as the resolution of the chemical map is driven largely by the energies where the optical constants vary rapidly.

In conclusion, soft x-ray ptychography is a powerful characterization technique that can offer both a higher spatial resolution than traditional x-ray transmission microscopy and also the capability to simultaneously map x-ray absorption and phase contrast of a material. The large phase shifts and strong energy dependence near atomic resonances play an important role not only in achieving high spatial resolution at single energies but also within the chemical composition map derived from multiple energies. This work establishes refraction-based spectro-microscopy, which can provide important insight into different materials characterization applications. For instance, in resonant soft x-ray scattering (RSOXS) techniques, usually $\delta$ is calculated through the Kramer-Kronig inversion of $\beta$ values obtained from NEXAFS measurements.\textsuperscript{30} X-ray refraction microscopy can readily provide experimental $\delta$ and $\beta$ values for any given morphology with high spatial and energy resolution compared to calculated values, hence acting as a powerful complementary technique.

See supplementary material for a brief description of the experimental system and data analysis protocol.

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