Mapping the Valence States of Transition-Metal Elements Using Energy-Filtered Transmission Electron Microscopy

Z. L. Wang,*† J. Bentley,‡ and N. D. Evans‡

School of Materials Science and Engineering Georgia Institute of Technology, Atlanta, Georgia 30332-0245, and Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6376

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The properties of transition-metal oxides are related to the presence of elements with mixed valences, such as Mn and Co. Spatial mapping of the valence-state distribution of transition-metal elements is a challenge to existing microscopy techniques. In this letter, using the valence-state information provided by the white lines observed in electron energy-loss spectroscopy in a transmission electron microscope (TEM), an experimental approach is demonstrated to map the valence-state distributions of Mn and Co using the energy-filtered TEM. An optimum spatial resolution of \( \sim 2 \text{ nm} \) has been achieved for two-phase Co oxides with sharp boundaries. This provides a new technique for quantifying the valence states of cations in magnetic oxides.

Many physical and chemical properties of inorganic materials are determined by the elements with mixed valences in the structural unit, by which we mean that an element has two or more different valences while forming a compound. Transition- and rare-earth-metal elements with mixed valences are unique for initiation of electronic, structural, and/or chemical evolutions. We have demonstrated previously the valence states of Mn and Co in their oxides by applying electron energy-loss spectroscopy (EELS) for quantitative determination. In EELS, the L ionization edges of transition-metal, rare-earth, and actinide compounds usually display sharp peaks at the near-edge region. These threshold peaks are known as white lines. The unoccupied 3d states form a narrow energy band, the transition of a 2p-state electron to the 3d levels, leading to the formation of white lines observed experimentally. EELS experiments have shown that a change in the valence states of cations introduces significant variation in the intensity ratio of the white lines, giving the possibility of identifying the occupation number of 3d or 4d electrons (or cation valence states) using the measured white line intensities.

The information obtained using EELS is an integration over the spatial region illuminated by the incident electron beam. In this paper, we introduce a new experimental approach which can give the distribution maps of cation valences in real space, allowing a direct identification of cations with different valence states. This is useful for studying nanocomposite magnetic oxide materials with mixed valences.

Experimental Section

Figure 1a shows an EELS spectrum of MnO\(_2\) acquired at 200 kV using a Hitachi HF-2000 transmission electron microscope equipped with a Gatan 666 parallel-detection electron energy-loss spectrometer. The oxygen K edge and the Mn L edge are clearly seen. The two sharp peaks are the L\(_3\) and L\(_2\) white lines, the intensity ratio of which is very sensitive to the valence state of Mn. The sharp white lines are the dominant EELS fine structures of transition- and rare-earth-metal elements. EELS analysis of the valence state is carried out in reference to the spectra acquired from standard specimens with known cation valence states. If a series of EELS spectra are acquired from several standard specimens with known valence states, an empirical plot of these data serves as the reference for determining the valence state of the element present in a new compound. Figure 1b shows a plot of the experimentally measured intensity ratios of white lines for Mn.

\[ \frac{\text{Intensity Ratio} \; \text{L}\_3/\text{L}\_2}{\text{Valence State of Mn}} \]

Figure 1. (a) EELS spectrum acquired from MnO\(_2\), showing the technique used to extract the intensities of white lines and the O–K edge. (b) Plot of the intensity ratios of L\(_3/L_2\) calculated from the spectra acquired from Mn compounds as a function of the cation valence. A nominal fit of the experimental data is shown by the solid curve.

1 Georgia Institute of Technology.
2 Oak Ridge National Laboratory.
observable thickness ranges. This is a key point in quantitative mapping of valence states.

In TEM, images formed by electrons with different energy losses can be formed, which is known as the energy-filtered TEM (EF-TEM). We have previously introduced this technique for mapping the distribution of surface-adsorbed organic molecules on Ag nanocrystal surfaces. The information provided by EF-TEM is mostly about the elemental distribution in a thin section of a specimen. To map the distribution of ionization states, an energy window 10 eV in width is required to isolate the L3 from L2 white lines. A five-window technique is introduced: two images are acquired at the energy losses prior to the L ionization edges, and they are to be used to subtract the background for the characteristic L-edge signals; two images are acquired from the L1 and L2 white lines, respectively; and the fifth image is recorded using the electrons right after the L2 line that will be used to subtract the continuous background underneath the L3 and L2 lines. Then, a L3/L2 ratio image will be obtained, which reflects the distribution of the valence state across the specimen. It must be pointed out that for most of the thickness range adequate for EELS analysis, the thickness effect has been removed in the L3/L2 image. The detailed experimental procedure for performing energy-filtered TEM can be found elsewhere.

To confirm the information provided by the L3/L2 images, the specimen composition is determined from the integrated intensities of the O–K and Mn–L2,3 ionization edges by

\[
\frac{n_O}{n_{Mn}} = \frac{I_O(\Delta)}{I_{Mn}(\Delta)} \frac{\sigma_{Mn}(\Delta)}{\sigma_O(\Delta)}
\]

where \(I_O(\Delta)\) and \(I_{Mn}(\Delta)\) are the integrated intensities of the O–K and Mn–L edges for an energy window \(\Delta\), respectively, above the ionization thresholds; \(\sigma_{Mn}(\Delta)\) and \(\sigma_O(\Delta)\) are the integrated ionization cross-sections for the corresponding energy window, and they can be calculated by the SIGMAK and SIGMAL programs in the hydrogen-like atomic model. From the energy-filtered images, the distribution map of the atomic ratio O/Mn can be calculated.

The MnO2 powders (grain size < 1 \(\mu\)m) was purchased from Aldrich Chemical Co., and they were dispersed in alcohol ultrasonically. The powders were supported by a thin carbon film and a Cu grid for TEM observation. The EF-TEM experiments were performed using a Philips CM30 (300 kV) TEM, equipped with a Gatan image filtering (GIF) system. This TEM provides the high beam current needed for chemical imaging. The energy window width was selected to be 10 eV, and it took 10–30 s (depending on specimen) exposure to acquire a single raw data image with a satisfactory signal-to-noise ratio. It took ca. 2–4.5 min to acquire a complete set of images, and it was important to ensure the least amount of drift of the specimen during data acquisition.

**Results**

To demonstrate the application of the EF-TEM for mapping valence states of transition-metal elements, a specimen containing phases with different valences is required. In reference to our previous studies of thermal-induced transition-metal oxides, a reduction of MnO2 was carried out in situ to a temperature of 350 °C, and the resulted reduced phases were a mixture of oxides of Mn with valences of 2+, 3+, and 4+. This is a model system to be used for mapping the valence-state distribution of Mn.

Figure 2 shows a series of images acquired by selecting the different energy-loss signals in EELS. From the conventional bright-field image given in Figure 2a, the crystal appears to be a single piece without typical characters. Energy-filtered images using the Mn–L2 and Mn–L3 lines (Figures 2b and 2c) show a distinct difference in the intensity distribution. After subtracting the image formed by the continuous energy-loss after the L2 white line, a ratio image of L3/L2 is attained (Figure 2d). A line scan across the image with an average of 50 pixels in width is given below the L3/L2 image, from which the distributions of Mn4+, Mn3+, and Mn2+ are unambiguously displayed in reference to the white line ratios exhibited in Figure 1b. The reduction of oxides first occurs at the surface region because of the easy desorption of the oxygen, while the core of the crystal is still MnO2.

On the other hand, a normalized image of (L3 + L2)/post line, calculated by dividing the (L3 + L2) image by the image acquired using the continuous energy-loss component after (post) the L2 line, shows no contrast variation across the specimen (Figure 2e). This result proves that the normalization technique introduced by Pearson et al. is less sensitive to the variation of the valence state. Therefore, the L3/L2 ratio image is likely
clearly indicates that the regions with Mn\textsuperscript{4+} concentrations, independent of specimen thickness. The image is worth pointing out that the O/Mn image is an image of atomic grain structure was chosen. The CoO and Co\textsubscript{3}O\textsubscript{4} phases are recorded from an agglomeration of MnO\textsubscript{2} in the valence-state mapping. Figure 3 shows a group of images to demonstrate the attainable spatial image resolution distribution.

The spatial resolution provided by EF-TEM depends strongly on the quality of the specimen. To give an optimum estimation, the O/Mn image is calculated from the images acquired from the valence-state map. A line scan across the valence-state map clearly illustrates that a spatial resolution of 2 nm can be achieved. This is remarkable in comparison to any existing techniques.

In conclusion, a new technique is presented for performing valence-state mapping of transition-metal elements using energy-filtered transmission electron microscopy. This technique gives an optimum spatial resolution of \( \sim 2 \text{ nm} \), and it directly reveals the valence distributions of Mn and Co. This type of information is remarkable for studying the physical chemistry of transition-metal oxides.

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**References and Notes**