Combinatorial Fluorescence XAFS Imaging of Manganese Complex Oxides

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This report demonstrates that novel XAFS (X-ray absorption fine structure) microimaging, which does not require any spatial scans of the sample, can be used to evaluate the chemical states of combinatorial array libraries. The method has been applied to manganese–cobalt spinel $MnCo_2O_4$ prepared on the same substrate under different synthesis conditions. The valence numbers of Mn have been studied as a map by obtaining X-ray fluorescence images (1000 × 1000 pixels) as a function of the incident energy of synchrotron X-rays. The advantage of this method is that the whole substrate, i.e., all samples in the library, can be observed in a short time, typically ca. 10 min, which is equivalent to the measuring time for a single sample on the substrate when conventional scanning methods are employed.

A combinatorial technique for inorganic material synthesis has been developed in order to discover promising new materials efficiently.[1] Materials are synthesized under different conditions in terms of chemical composition and/or processing temperature on a small substrate in parallel, and various products can be obtained in a much shorter time than before. X-ray fluorescence (XRF) analysis[2,3] is one of the methods used to screen desired products. In order to see an element-map of the given combinatorial library, point-by-point XRF analysis using a microbeam of focused X-rays from synchrotron radiation (SR)[2] or from an X-ray tube equipped with a polycapillary optic[3] has been employed so far. Characterization is possible, but one possible problem is that even with a highly brilliant synchrotron source, quite a long measuring time (e.g., at least several hours, typically half a day) is required. Alternatively, a projection-type X-ray imaging method,[4,5] which uses quite a wide beam and does not require any spatial scans of the sample, is a good candidate for performing combinatorial imaging very quickly. XRF analysis provides information not only on the chemical composition, but also on the chemical states of the constituent atoms and the local atomic arrangements by means of an incident X-ray energy scan to observe XAFS (X-ray absorption fine structure).[6]

The samples studied were $MnCo_2O_4$, which has spinel structure and shows good catalytic activity with respect to the oxygen-reduction reaction utilized for the cathode in alkaline fuel cells or air batteries. From the viewpoint of such catalytic applications, preparing ultrafine particles is extremely important, and low-temperature synthesis, which can suppress growth of large grains, is promising.[7] Lowering the temperature appears to be an important direction in reducing the particle size, but there have been several questions. One of the problems here is that the oxidation states and distribution of transition metals in the spinel structure can be changed even if the crystal structure of the materials is as expected. Therefore, it is important to find the optimum lowest temperature to obtain the right $MnCo_2O_4$. In the present study, a combinatorial library composed of nine samples has been prepared by a synthesis method using low-temperature decomposition of salts.[8] Three kinds of aqueous solutions containing (1) 0.25 M $MnCl_2$ and 0.5 M $CoCl_2$, (2) 0.25 M $MnCl_2$, 0.5 M $CoCl_2$, and 1.6 M HNO_3, and (3) 0.25 M $MnCl_2$, 0.5 M $CoCl_2$, and 8 M HNO_3, respectively, were prepared. Three sets of three kinds of 0.5 µL drops were put on an alumina substrate, and each set was heated on a hot plate at 350, 285, and 220 °C, respectively. Then, nine spots of the separate products—3(HNO_3 concentrations) × 3(temperatures)—were prepared in an 8.5-mm square area after drying.

The XRF experiment was performed at BL-16A1 of Photon Factory, KEK in Tsukuba, Japan. Highly brilliant synchrotron radiation X-rays from the multipole wiggler source were monochromatized by a Si(111) double crystal, and a homogeneous wide beam (0.6 (V) × 20 (H) mm^2) was taken to irradiate the entire surface of a tabular combinatorial substrate in low-angle geometry (less than around 2 deg). The energy dispersion of the X-ray beam is in the order of 0.1 eV, i.e., negligibly small, and, therefore, all the samples are irradiated by X-ray photons with the same energy. The XRF thus generated is detected by a two-dimensional detector—here a CCD camera, which has a collimator plate inside. The CCD camera is set extremely close to the substrate surface, leaving only a gap for incident X-rays. Further technical details of the projection-type X-ray microscope can be found elsewhere.[4–6]

As shown in Figure 1, a 2-D XRF image was observed for a combinatorial library of $MnCo_2O_4$ at the incident X-ray energy 6570 eV (just above the Mn K edge) with an exposure time of only 1 s. The image is of an 8 × 8 mm^2 (1000 × 1000 pixels)

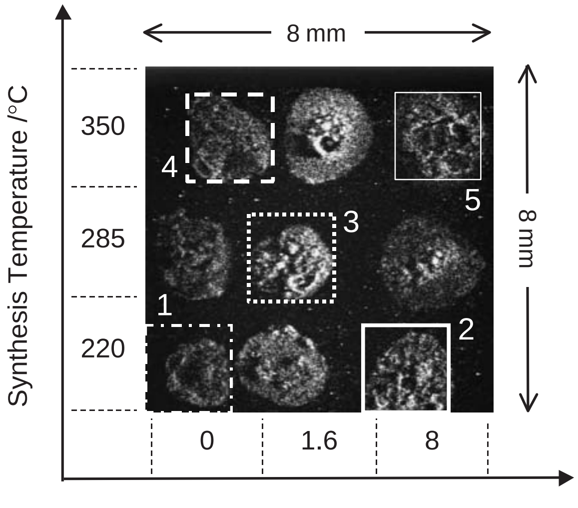

Figure 1. XRF image of $MnCo_2O_4$ combinatorial library. Nine spots of the products obtained by varying HNO_3 concentration in the reactant solution and heating conditions are shown.

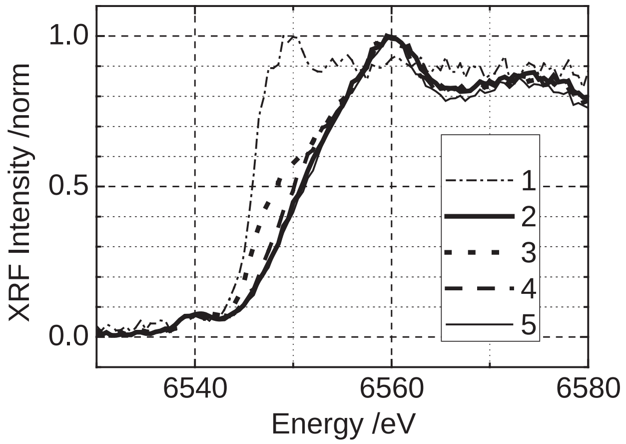

Figure 2. Mn K XAFS spectra obtained from 100 images sequentially obtained as a function of incident X-ray energy.

area, and the spatial resolution is around 20 µm. One can see that each product is identified as a bright spot. Imaging was repeated during the monochromator scans from 6530 to 6580 eV with 0.5 eV steps (around Mn K edge). The XRF intensity of each product was calculated by integrating the intensities in the corresponding image pixels. The XAFS spectrum for each of the nine products can be obtained by plotting the XRF intensity of each energy point around the Mn K edge.

The XRF intensities of five of the nine products calculated by the integration of the square areas in Figure 1 (described as 1, 2, 3, 4, and 5) were plotted in Figure 2. Here, each spectrum was normalized so as to compare the shifts of the absorption edges and other spectral features. It was found that spectrum "1" resembles that of $MnCl_2{\cdot}nH_2O$, while spectra "2", "4", and "5" are close to that of $MnCo_2O_4$. The spectra "3" seems of the intermediate stage. The swelling of the shoulder in "4" around 6550 eV is notable in the three $MnCo_2O_4$ profiles "2", "4", and "5". This suggests that synthesis without additive HNO_3 results in a similar chemical state to that obtained via treatment at high temperature (e.g. 800 °C). That is, the concentration of HNO_3 is important because it exerts an influence on the manganese chemical states.

As shifts of the absorption edge are sensitive to the chemical state, imaging can be used to see which synthesis conditions in the combinatorial library are successful for obtaining the goal material of $MnCo_2O_4$. The XRF image was converted to a 50×50-block image by integration of 20×20 pixels, and the midpoint energy of the μt jump was computed one by one for each block. In Figure 3, the distribution of the absorption-edge shift was drawn as a 50×50-block (new pixel) image. Though some pixels show false signals in the image, for example, some are from the bare substrate without samples, the image corresponds mainly to the distribution of the manganese state on the substrate. As shown in the image, as both the concentration of HNO_3 and heating temperature increase, the chemical shift becomes larger, indicating a higher oxidation number. It became clear that either concentrated HNO_3 ($\approx$8 M) or a higher temperature (ca. 350 °C) is important for obtaining $MnCo_2O_4$. By image observation, the combinatorial substrate could be characterized in a visually easy-to-understand way in a short time, and, therefore, in an efficient manner.

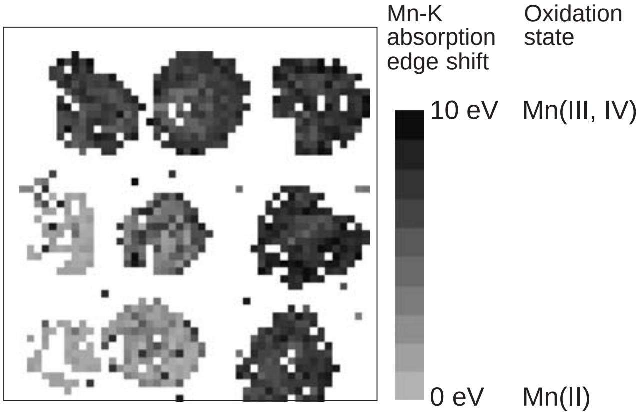

Figure 3. Mn K absorption-edge shift image (50×50 pixels) of $MnCo_2O_4$ combinatorial library. The shift is large for dark pixels and small for light pixels. The shift amount is based on the absorption edge of divalent Mn (6545 eV for MnO). The XRF signals of white pixels are not intense enough for precise extraction of XAFS spectra.

In summary, the present results have demonstrated that multiple products of functional materials arranged on a combinatorial library are effectively evaluated by a novel XAFS microimaging method. The reaction condition in which $MnCo_2O_4$ is obtained at low temperature could be examined. The lowest temperature at which $MnCo_2O_4$ can be produced via decomposition of chlorides is around 350 °C. Although the addition of concentrated HNO_3 can lower the temperature to 220 °C or so, the chemical state and consequently the functionality of the product as a cathode material are different from those produced without HNO_3 or via treatment at high temperature. The technique seems very promising for combinatorial material research on more practical systems.

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