Ultra-high resolution EEL studies of domains in Perovskite

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Abstract. Lamella-type planar features in La\textsubscript{0.6}Ca\textsubscript{0.4}CoO\textsubscript{3} were investigated in the NorthWest STEM and the Daresbury SuperSTEM. Structural and chemical information was obtained by combining EEL spectrum- and atomic resolution HAADF Z-contrast imaging. The domains appear to be $\frac{1}{2}$-unit-cell-wide Ca-enriched lamellae of the rock salt structure, faultlessly embedded into the Perovskite lattice.

1. Introduction

Perovskite-type metal oxides are used as low-cost electrocatalysts in fuel cells and metal/air batteries\textsuperscript{1}. The perovskite type oxide (ABO\textsubscript{3}) has a rare earth and/or alkaline earth ion in A and transition metals in B. Here A = La\textsubscript{0.6}Ca\textsubscript{0.4} and B = Co (LCCO). The current idea of its function in the battery is that upon substitution of the 3-valenced rare earth element by a 2-valenced alkaline earth element the transition metal would be partly oxidised, in the case of Co to the unusual 4+ state. As Co\textsuperscript{4+}, however, is not stable it would then have to be reduced by lattice oxygen\textsuperscript{2}, resulting in oxygen vacancies, hence the use as oxygen-diffusion- or air-electrode. In order to study the mechanism of oxygen reduction/evolution it is desirable to have electrodes of good crystalline quality with well-defined electrolyte/oxide interfaces. In this study single crystalline films grown on inactive substrates by pulsed-laser deposition were used, details of growth and crystallographic characterisation have previously been reported\textsuperscript{3,4}. TEM has shown that sub-stoichiometric films, and films that have undergone electrochemical cycling, exhibit narrow domains of only one lattice plane distance, proceeding parallel to the \{001\}. The purpose of this study was to affirm whether the domain contrast is indeed related to local changes in the Co oxidation state or the occurrence of oxygen vacancies.

2. Experimental

The sample was a [110] cross section made from a La\textsubscript{0.6}Ca\textsubscript{0.4}CoO\textsubscript{3} film, epitaxially grown on to a [100] MgO substrate\textsuperscript{3,4}. The analysis was carried out in two dedicated cold field emission scanning transmission electron microscopes (STEMs), equipped with UHV Enfina electron energy loss (EEL) systems, the Liverpool NorthWest STEM, and the Daresbury SuperSTEM. The latter is the first UK C\textsuperscript{5} corrected STEM, which employs a Nion MarkII quadrupole-octupole corrector\textsuperscript{5}. It allows one to carry out high angle annular dark field (HAADF) Z-contrast lattice imaging\textsuperscript{6}, and atomic column EEL spectroscopy with 1 ångström resolution.
3. Results and Discussion

Figure 1 (top) shows spectra of a spectrum image (SI), one pixel in width and 25 pixels in length, with pixel size 0.24 nm, recorded in the NorthWest STEM. The SI constitutes in effect an EEL line scan, taken perpendicularly across the domains. The e-beam was incident along [1-10] (see fig. 2, middle, for crystal orientation relationships). The spectra are superposed on an HAADF image, which shows two domains exhibiting slightly darker contrast. Domains appear often grouped as two or three, interspaced by one or two perovskite unit cells. The spectra taken on the domains show that the small peak at the onset of the O-K edge is suppressed. The e-probe was just below 1 nm, so these are not atomic column resolution EELS spectra. Hence the spectra result from a convolution of the characteristics of the domain- and the neighbouring perovskite. Nevertheless changes in the O-edge, as well as an increase in the Ca-signal, are notable at the domain. The bottom right hand panel of fig. 1 shows the differences in the O-K-edge fine structure of spectra taken of the planar defect and the close-by bulk more closely. These data are of the domain shown in fig. 2. They were extracted from an SI line scan conducted in a similar fashion to that in the top panel, but they were taken in the SuperSTEM with a 1-Å probe. The O-edge of bulk CaO is included for reference. Although, again, the differences between domain and bulk spectrum could be observed directly in the raw data, the domain spectrum (middle spectrum, fig.1) was enhanced by subtracting a fraction of a perovskite bulk spectrum (of a pixel at the end of the scan line). The line scan pixel corresponding to the centre of the domain could unambiguously be identified, because the Ca-edge intensity was at maximum here. The reason for constructing a difference spectrum was that non-domain scattering contributed to the as- measured domain spectrum. Although the highly localised electron probe couples into individual atomic columns and will therefore undergo very little broadening on traversing the (sufficiently thin) sample, there will still be sufficient de-coupling when the probe is not located accurately on the columns. This was difficult to achieve during EEL line scans, primarily due to spatial drift during the scan period, even if this is at the sub-Ångström level. So partial probing of the adjacent columns is to be expected. Hence the spectrum taken on the ~2.4 Å wide domain will be influenced by the perovskite lattice planes on either side. The fraction of the bulk spectrum contribution was established as the factor by which the bulk spectrum had to be scaled so that the peak at 531.5 eV vanished upon
subtraction from the as-measured domain spectrum. This peak, resulting from 3d-2p hybridisation, does not occur in rock salt.

Figure 2 shows an unprocessed HAADF lattice image, including a domain, similar to those in the lower resolution HAADF image in fig 1 (top). The curves represent the integrated counts in energy windows set around the Ca-, O-, La and Co- absorption edge in background subtracted EEL spectra of the line scan SI. The scan length was about 20 Å, with a step separation of ~0.7 Å, resulting in ~30 positions (pixels), in which spectra were taken. Line scans were carried out in exactly the same position for the energy regime (a) ~300-600 eV (Ca-L- and O-K-edge), and (b) ~650-950 eV, (Co-L- and La-M edge). The white intensity profiles in fig. 2 were obtained from an a-, and the black profiles from a b-regime line scan SI. As in fig. 1 (top) the Ca notably shows enhancement in the domain, counteracted by the Co, whereas trends in the O and La are less visible. No adjustment of the intensity profiles has been made for thickness variations in the sample, hence the underlying slope in the Ca. The average counts in the perfect perovskite lattice of all elements were scaled to the same ‘height’ when profiles were superposed, so the relative elemental fluctuations across the domain can be directly compared. For clarity in fig. 2 the profiles are vertically shifted. The count statistics are sufficient to ascertain that the undulations in the O, La and Co counts along the scan line are a true reflection of the atomic positions of these elements: in the perfect perovskite lattice positions of La containing columns with the brightest contrast in the HAADF image show also the highest La-counts in the EEL profile. Positions of Co-containing columns with medium contrast values (between the bright blobs) coincide with the highest Co-counts in the EEL profile. O-columns in positions of the darkest contrast patches give the highest O-counts. Although there is also O in the La (Ca)-O planes, its amount is twice as high in the Co-O planes, hence the relative enhancement in the latter. The bottom of the troughs in the Co-profile signifies the contrast levels in positions where there is no Co. In the domain the contrast level is even lower then that between the Co-columns, furthermore the separation of the A-type atoms is considerably smaller across the domain. Both observations lead to the conclusion that the Co-column and hence the B-atom plane is missing here. Ca is enriched in the A-atom planes. With its much lower Z then La, it will not contribute much to the contrast of these planes, which is dominated by the La. However, a general decline in brightness of the bright rows on either side of the domain can be noted in fig. 2. This, together with the Ca-increase in the EEL profile,
is an indication for a substantial substitution of La by Ca in the two adjacent A-planes at the domain.
Inspection of each individual spectrum in the line scan image showed that there is no change in the
Co-oxidation state: the energy position of the Co-absorption edge and its shape stayed the same.
This information together with the rock salt-type EEL spectrum at the domain suggests that a ½ unit
cell slice of the rock salt structure is embedded in the perovskite lattice. The (010) rock salt planes
 correspond to the (110) planes in the perovskite with very similar spacing (~0.25 nm). The [001] rock
salt planes (parallel to the domain) coincide with A-atom planes of the perovskite structure, whose
distance to the B-atom planes is 0.18 nm. However, as the domain intersects the entire film, it can
assume its own rock salt spacing. So each domain constitutes a missing B-atom plane leaving two A-
atom planes next to each other, displaced by a $\frac{1}{2} \frac{1}{2} 0$ rigid body shift to enable ionic bonding. The
rigid body shift will not be seen in the lattice images, as it manifests itself only in a swap of the A-type
and O atoms in the columns. Gu and Čeh have reported on faults of the rock salt structure in CaTiO$_3$.

We modelled EEL profiles by a simple empirical model. The elemental concentrations were
represented by peaks of the form $S(r-r_i) = x \left( \frac{1}{\sqrt{2\pi} \sigma} \right) \exp \left\{ -\frac{(r-r_i)^2}{\sigma^2} \right\} \exp \left\{ -w(r-r_i) \right\}$, where $\bullet$ denotes
convolution and $r_i$ the atomic positions. The occupancy of A-atom sites was $x = 0.4$ (La$_{1-x}$Ca$_x$) off the
domain, and $x = 0.4...1$, varied in steps of 0.1, on the domain. The first function in $S$, a Gaussian,
provides the high frequency limit of the spatial resolution, the second function imposes an exponential
tail, which accounts for beam aberration and probe spreading. The chosen values for $\sigma$ and $w$ reflect
the instrument performance. Figure 2 (right) shows modelled EEL profiles and concentration ratios for
different domain stoichiometries along with experimental data (note the y-scale is arbitrary due to the
undetermined constant $A$). The Co/La ratio at the domain is enhanced for a pure CaO domain due to
the shape of $S$. In this case no La atom sits closer to the domain then the Co in the closest occupied B-
sites, and thus the spatially broadened Co-signal overrules the La signal at the domain. In a domain
with A-site occupancy of the bulk stoichiometry ($x = 0.4$), there is a distinct drop in the Co/La ratio.
However, the experimental results indicate a moderate drop. Also, whereas the Ca signal increases in
absolute terms, the La-signal does not. This can be explained by a significant increase, but not a
complete substitution, of Ca at the domain; the modelled profiles agree best with the measured data for
$0.7 < x < 0.8$.

In summary we demonstrated, via highly spatially resolved EELS, in combination with EELS
modelling and atomic resolution HAADF imaging, that the Ca undergoes segregation into domains,
where it is enriched by a factor of 2 compared to the bulk. As a result of missing Co-O planes the
domains consist of two adjacent Ca-enriched A-atom planes, shifted by $\frac{1}{2} \frac{1}{2} 0$ with respect to each
other. They constitute therefore ½ -unit-cell-wide rock salt lamellae. The fact that Ca and Co are not
uniformly distributed, and also that Co is not present in the 4+ state might suggest restrictions in the
oxygen diffusion and hence the functioning of the electrode.

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