Supplementary Information

The Relationship Between Mn Oxidation State Changes and Oxygen Reduction Activity in (La,Ca)MnO3 as Probed by In Situ XAS and XES

Veronica Celorrio1\*, Andrew S. Leach2, 3, Haoliang Huang2, Shusaku Hayama1, Adam Freeman1, David W. Inwood2, David J. Fermin4\*, Andrea E. Russell2\*.

1Diamond Light Source Ltd. Diamond House. Harwell Campus. Didcot, OX11 0DE, UK.

2School of Chemistry, University of Southampton. Highfield, Southampton, SO17 1BJ UK.

3Current address: Electrochemical Innovation Lab, Department of Chemical Engineering, University College London, London WC1E 7JE, UK. The Faraday Institution, Harwell Science and Innovation Campus, Didcot OX11 0RA, UK.

4School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, UK.

**Corresponding authors:**

\*Email: [Veronica.Celorrio@diamond.ac.uk](mailto:Veronica.Celorrio@diamond.ac.uk) (VC)

\*Email: [David.Fermin@bristol.ac.uk](mailto:David.Fermin@bristol.ac.uk) (DJF)

\*Email: [a.e.russell@soton.ac.uk](mailto:a.e.russell@soton.ac.uk) (AER)



**Figure S1.** Percentage of peroxide formation during ORR calculated by using the disc and ring currents. The yield is calculated as from:

Eq. S.1

Where *iD* is the disc current, *iR* is the ring current and *N* is the collection coefficient (0.42).



**Figure S2.** Normalised XANES spectra at the Mn K-edge of the standards MnO, Mn2O3 and MnO2 oxides.



**Figure S3.** Calibration plot for the determination of the average Mn oxidation state from the edge positions, including edge positions of the LaMnO3 (a) and CaMnO3 (b) electrodes as a function of the potential.



**Figure S4.** Normalized Mn K-edge XANES spectra. The inset shows the Mn K pre-edge feature compared with those of the reference materials (a). Data (color line) and fits (black line) of the k3-weighted EXAFS signals in *k*-space for LaMnO3 and CaMnO3 powder pellets (b). Data (color lines) and fits (black lines) of the magnitude (c) and real part (d) of FT signal of the k3-weighted EXAFS. LaMnO3: 2.6 < k <11.0 Å-1, 1.0 < R < 4 Å. CaMnO3: 3.0 < k <12.0 Å-1, 1.0 < R < 4.0 Å.

Figure S4a contrasts the normalized Mn K-edge XANES spectra of LaMnO3 and CaMnO3 nanoparticles. The main Mn K-edge in the case of LaMnO3 is shifted by 4 eV to lower energies in comparison to CaMnO3. A similar difference is observed between MnO2 and Mn2O3 standards (Figure S2), which is consistent with Mn3+ and Mn4+ oxidation states.[25-26](#_ENREF_25) The inset in Fig. S4a shows the comparison of the position of the pre-edge features compared with that of the references, indicating for LaMnO3 the pre-edge is positioned at the same energy than that for Mn2O3, whereas the CaMnO3 pre-edge is at the same energy than that for MnO2. Figure S4b shows the comparison between the Fourier transform (FT) of the experimental spectra (empty circles) and the best-fit simulations (coloured lines) for LaMnO3 and CaMnO3 (*k*-space data is shown Figure S2). The first peak at around 1.5 Å (without phase correction) corresponds to the first coordination shell (Mn–O). The second peak, above 3 Å, is associated with the second shell, which is a combination of Mn–La, Mn–Mn single scattering together with multiple scattering Mn–O paths. The starting model to fit the data was constructed using unit cells as deduced from the XRD Rietveld refinement, and the coordination numbers fixed to their crystallographic values. The amplitude reduction factor (S02), bond lengths, Debye-Waller factors (σ2) and the energy shift parameter (ΔE0) were refined. The best-fit parameters are summarized in Table S1.



**Figure S5.** Data recorded at the Mn K edge for the dry electrodes (*ex situ*). Data (color line) and fits (black line) of the k3-weighted EXAFS signals in *k*-space for LaMnO3 (a) and CaMnO3 (d). Data (color lines) and fits (black lines) of the magnitude (b, e) and real part (c, f) of FT signal of the k3-weighted EXAFS. LaMnO3: 2.6 < k < 11.0 Å-1; 1.1 < R < 4.0 Å. CaMnO3: 3.0 < k < 12.0 Å-1; 1.0 < R < 4.0 Å.



**Figure S6.** Datarecorded at the Mn K edge and at 1.4 V vs RHE. Data (color line) and fits (black line) of the k3-weighted EXAFS signals in *k*-space for LaMnO3 (a) and CaMnO3 (d). Data (color lines) and fits (black lines) of the magnitude (b, e) and real part (c, f) of FT signal of the k3-weighted EXAFS. LaMnO3: 2.6 < k < 11.0 Å-1; 1.1 < R < 4.0 Å. CaMnO3: 3.0 < k < 12.0 Å-1; 1.0 < R < 4.0 Å-1.



**Figure S7.** First shell analysis of data recorded at the Mn K edge and under different potential conditions. Data (black lines) and fits (red lines) of the k3-weighted EXAFS signals in *k*-space for LaMnO3 (a) and CaMnO3 (d). Data (black lines) and fits (red lines) of the magnitude (b, e) and real part (c, f) of FT signal of the k3-weighted EXAFS. LaMnO3: 2.6 < k < 10.9 Å-1; 1.1 < R < 2.2 Å. CaMnO3: 2.5 < k < 10.1 Å-1; 1.0 < R < 2.2 Å.



**Figure S8.** HERFD-XANES spectra measured with the spectrometer set at the peak of Kβ1,3 line of the MnO2, Mn2O3 and MnO standard samples.



**Figure S9.** Normalized Mn Kβ XES spectra of the MnO2, Mn2O3 and MnO standard samples. All the Kβ XES spectra were measured well above the absorption edge of Mn.

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**Figure S10.** Linear combination of the normalized Mn Kβ XES spectra for LaMnO3 (top a - c) and CaMnO3 (bottom d - f) at the different potentials under study: 1.4 V (a, d), 0.5 V (b, e) and 0.2 V (c, f).



**Figure S11.** Ex situ X-ray powder diffraction measured before and after electrochemistry for LaMnO3 (a) and CaMnO3 (b). The post mortem XRD were collected on the dried electrodes after the XES and HERFD-XANES measurements. Whereas there is no significant change for LaMnO3 (the particle size calculated from the width of the (111) peak (~32°) remains the same after the electrochemical cycle) additional peaks appear in the XRD of the CaMnO3. The new features correspond to a MnO2 phase. However, as the XES fits (Figs. 6 and S11) show that Mn2+ state is a product of the electrochemical reduction, this result is misleading and may arise from subsequent exposure to air and drying out of the catalyst electrode



**Figure S12.** Cyclic voltammograms of the LaMnO3 and CaMnO3 electrodes in Ar-saturated 0.1 M KOH solution at 0.002 V s-1 before and after the AST. No change on electrochemical signals was observed for LaMnO3 after the AST. For CaMnO3, the reduction peak at 0.8 V shifts to more negative potentials to ~0.65 V after being subjected to AST.



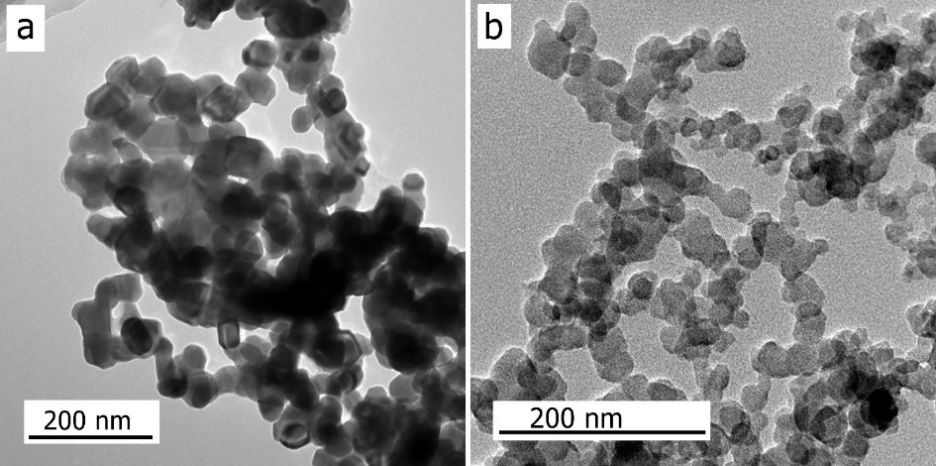
**Figure S13.** Analysis of data recorded at the Mn K edge and after the accelerated stress test (AST). Data (color lines) and fits (black lines) of the k3-weighted EXAFS signals in *k*-space for LaMnO3 (a) and CaMnO3 (d). Data (color lines) and fits (black lines) of the magnitude (b, e) and real part (c, f) of FT signal of the k3-weighted EXAFS. LaMnO3: 2.6 < k < 11.0 Å-1; 1.1 < R < 4.0 Å. CaMnO3: 2.6 < k < 1001 Å-1; 1.0 < R < 2.0 Å.



**Figure S14.** Ex situ X-ray powder diffraction measured before and after the accelerated stress tests (AST) for LaMnO3 (a) and CaMnO3 (b).



**Figure S15.** XRD patterns of as-synthesized LaMnO3 (a) and CaMnO3 (b). Red dots correspond to the experimental values while the thin black line corresponds to the Rietveld refinement. The blue line shows the difference between the experimental and refined patterns. The green bars correspond to the positions of the allowed Bragg reflections for the main phase. LaMnO3 (a) was accurately refined in the cubic lattice with the space group Pm3m (the relatively broad XRD features arising from the small particle sizes may introduce a degree of uncertainty), whereas an orthorhombic Pnma space group was employed to explain the structure of CaMnO3 (b). Structural parameters were obtained by the Rietveld method and can be found in Supplementary Table 8.



**Figure S16.** Representative transmission electron micrographs of LaMnO3 (a) and CaMnO3 (b) oxide nanoparticles. Analysis of over 100 particles in each sample image yielded mean particle sizes of 13.2 ± 2.6 nm for LaMnO3 and 25.9 ± 4.3 nm for CaMnO3.

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**Figure S17.** Schematic view of the I20-Scanning branch of Diamond Light Source.

**Table S1.** Relative energy shift and the best fit results from the structural analysis of LaMnO3 and CaMnO3 powder pellets at the Mn K-edge. N is the coordination number, RMn-O is the interatomic distance and σ2 is the Debye-Waller factor. Rf is the R-factor, which represents the relative error of the fit and data. LaMnO3 fitting range 2.6 < k <11.0 Å-1, 1.0 < R < 4 Å. CaMnO3 fitting range 3.0 < k <12.0 Å-1, 1.0 < R < 4.0 Å.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | Shell | N | R / Å | σ2 x 103 / Å2 | ΔE0 / eV | S02 | Rf |
| CaMnO3 | Mn-O1 | 6 | 1.89 ± 0.01 | 2.7 ± 1.1 | -5.3 ± 1.5 | 0.69 ± 0.07 | 0.023 |
| Mn-Ca | 8 | 3.21 ± 0.03 | 14.9 ± 2.5 |
| Mn-Mn2 | 6 | 3.73 ± 0.03 | 8.3 ± 2.3 |
| LaMnO3 | Mn-O1 | 6 | 1.91 ± 0.01 | 4.1 ± 1.1 | -3.8 ± 0.9 | 0.53 ± 0.05 | 0.015 |
| Mn-La1a | 2 | 3.20 ± 0.07 | 6.4 ± 6.3 |
| Mn-La1b | 6 | 3.33 ± 0.04 |
| Mn-Mn2 | 6 | 3.69 ± 0.06 | 3.4 ± 0.3 |

**Table S2.** Relative energy shift and the best fit results from the structural analysis of LaMnO3 and CaMnO3 dry electrodes at the Mn K-edge. N is the coordination number, RMn-O is the interatomic distance and σ2 is the Debye-Waller factor. Rf is the R-factor, which represents the relative error of the fit and data. LaMnO3: 2.6 < k < 11.0; 1.1 < R < 4.0. CaMnO3: 3.0 < k < 12.0; 1.0 < R < 4.0.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | Shell | N | R / Å | σ2 x 103 / Å2 | S02 | ΔE0 / eV | Rf |
| CaMnO3 | Mn-O1 | 6 | 1.89 ± 0.01 | 1.4 ± 0.9 | 0.48 ± 0.04 | -4.8 ± 1.4 | 0.024 |
| Mn-Ca | 8 | 3.20 ± 0.03 | 16.1 ± 2.8 |
| Mn-Mn2 | 6 | 3.72 ± 0.03 | 6.5 ± 2.0 |
| LaMnO3 | Mn-O1 | 6 | 1.91 ± 0.01 | 2.8 ± 0.9 | 0.43 ± 0.03 | -2.7 ± 0.6 | 0.012 |
| Mn-La1a | 2 | 3.19 ± 0.11 | 10.4 ± 2.1 |
| Mn-La1b | 6 | 3.36 ± 0.03 |
| Mn-Mn2 | 6 | 3.67 ± 0.03 | 10.9 ± 5.3 |

**Table S3.** Relative energy shift and the best fit results from the structural analysis of LaMnO3 and CaMnO3 at the Mn K-edge and at 1.4 V vs RHE. N is the coordination number, RMn-O is the interatomic distance and σ2 is the Debye-Waller factor. Rf is the R-factor, which represents the relative error of the fit and data. LaMnO3: 2.6 < k < 11.0; 1.1 < R < 4.0. CaMnO3: 3.0 < k < 12.0; 1.0 < R < 4.0.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | Shell | N | R / Å | σ2 x 103 / Å2 | ΔE0 / eV | Rf |
| CaMnO3  (S02 = 0.48) | Mn-O1 | 6 | 1.89 ± 0.01 | 1.1 ± 0.5 | -5.3 ± 1.4 | 0.033 |
| Mn-Ca | 8 | 3.17 ± 0.04 | 22.5 ± 4.4 |
| Mn-Mn2 | 6 | 3.70 ± 0.03 | 6.6 ± 1.9 |
| LaMnO3  (S02 = 0.43) | Mn-O1 | 6 | 1.90 ± 0.01 | 4.5 ± 0.8 | -5.3 ± 1.1 | 0.028 |
| Mn-La1a | 2 | 3.18 ± 0.11 | 6.4 ± 5.1 |
| Mn-La1b | 6 | 3.29 ± 0.03 |
| Mn-Mn2 | 6 | 3.69 ± 0.03 | 2.3 ± 1.3 |

**Table S4.** Relative energy shift and the best fit results from the structural analysis of the first coordination shell of LaMnO3 and CaMnO3 at the Mn K-edge and at the different potential conditions. N is the coordination number, RMn-O is the interatomic distance and σ2 is the Debye-Waller factor. Rf is the R-factor, which represents the relative error of the fit and data. LaMnO3: 2.6 < k < 10.9 Å-1; 1.1 < R < 2.2 Å. CaMnO3: 2.5 < k < 10.1 Å-1; 1.0 < R < 2.2 Å.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| LaMnO3 (S02 = 0.43) | | | | | | |
| Potential | Scattering | CN | R / Å | σ2 / Å2 | ΔE0 / eV | Rfactor |
| 1.4 V vs RHE | Mn–O | 4.9 ± 1.2 | 1.90 ± 0.03 | 3.6 ± 2.8 | -6.1 ± 3.1 | 0.026 |
| 0.7 V | Mn–O | 5.0 ± 1.4 | 1.90 ± 0.04 | 3.9 ± 3.6 | -6.1 ± 3.5 | 0.039 |
| 0.5 V | Mn–O | 4.8 ± 1.2 | 1.90 ± 0.04 | 3.6 ± 3.6 | -6.3 ± 3.3 | 0.034 |
| 0.2 V | Mn–O | 3.8 ± 1.2 | 1.88 ± 0.05 | 4.5 ± 4.3 | -9.9 ± 4.6 | 0.045 |
| CaMnO3 (S02 = 0.48) | | | | | | |
| 1.4 V vs RHE | Mn–O | 4.7 ± 1.2 | 1.87 ± 0.03 | 3.1 ± 1.1 | -6.6 ± 3.3 | 0.026 |
| 0.7 V vs RHE | Mn–O | 4.2 ± 1.4 | 1.88 ± 0.04 | 3.9 ± 0.8 | -7.1 ± 4.0 | 0.043 |
| 0.5 V vs RHE | Mn–O | 3.0 ± 1.0 | 1.88 ± 0.04 | 3.9 ± 0.9 | -8.6 ± 4.5 | 0.044 |
| 0.2 V vs RHE | Mn–O | 3.2 ± 0.8 | 2.24 ± 0.05 | 5.2 ± 4.9 | 2.7 ± 2.7 | 0.036 |

**Table S5.** Results of the linear combination analysis of LaMnO3 and CaMnO3 XES spectra at different potentials by the references MnO2, Mn2O3 and MnO.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Potential (V) | LaMnO3 | | | | CaMnO3 | | | | |
| % Mn4+ | % Mn3+ | % Mn2+ | Average Mn oxidation state | % Mn4+ | % Mn3+ | % Mn2+ | Average Mn oxidation state |
| No potential | 56 ± 2 | 32 ± 6 | 11 ± 4 | 3.4 | 89 ± 2 | 19 ± 5 | 1 ± 3 | 4.1 |
| 1.4 | 71 ± 3 | 11 ± 7 | 17 ± 4 | 3.5 | 89 ± 2 | 10 ± 6 | 2 ± 4 | 3.9 |
| 0.5 | 39 ± 2 | 51 ± 5 | 10 ± 3 | 3.3 | 70 ± 2 | 31 ± 4 | 0 ± 3 | 3.7 |
| 0.2 | 24 ± 2 | 58 ± 5 | 18 ± 3 | 3.1 | 8 ± 5 | 66 ± 14 | 26 ± 9 | 2.8 |

**Table S6.** Error numbers for fits of Mn Kβ1,3 XES spectra for LaMnO3 and CaMnO3 as a function of potential.

|  |  |  |
| --- | --- | --- |
| Potential (V) | LaMnO3 | CaMnO3 |
| Adj. R-Square | Adj. R-Square |
| No potential | 0.99040 | 0.99970 |
| 1.4 | 0.99943 | 0.99961 |
| 0.5 | 0.99963 | 0.99977 |
| 0.2 | 0.99966 | 0.99761 |

**Table S7.** Relative energy shift and the best fit results from the structural analysis of CaMnO3 at the Mn K-edge and after the accelerated stress test. N is the coordination number, RMn-O is the interatomic distance and σ2 is the Debye-Waller factor. Rf is the R-factor, which represents the relative error of the fit and data. LaMnO3: 2.6 < k < 11.0; 1.1 < R < 4.0. CaMnO3: 2.6 < k < 10.0; 1.0 < R < 2.0.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | Shell | N | R / Å | σ2 x 103 / Å2 | S02 | ΔE0 / eV | Rf |
| CaMnO3  (S02 = 0.48) | Mn-O | 4.0 ± 1.4 | 1.88 ± 0.04 | 4.3 ± 1.7 | --- | -8.1 ± 4.7 | 0.020 |
| LaMnO3 | Mn-O1 | 6 | 1.90 ± 0.01 | 3.1 ± 0.8 | 0.45 ± 0.03 | -4.1 ± 0.6 | 0.007 |
| Mn-La1a | 2 | 3.44 ± 0.08 | 11.1 ± 5.3 |
| Mn-La1b | 6 | 3.25 ± 0.02 |
| Mn-Mn2 | 6 | 3.65 ± 0.01 | 6.8 ± 1.3 |

**Table S8.** Unit cell parameters and statistics obtained from Rietveld refinement of the XRD patterns.

|  |  |  |
| --- | --- | --- |
|  | LaMnO3 | CaMnO3 |
| Space Group | *Pm3m* | *Pnma* |
| a [Å] | 3.887(3) | 5.277(1) |
| b [Å] | 3.887(3) | 7.443(5) |
| c [Å] | 3.887(3) | 5.265(3) |
| χ2 | 3.21 | 1.65 |
| Rp [%] | 2.05 | 1.28 |
| Rwp [%] | 2.75 | 1.71 |
| Rexp [%] | 1.53 | 1.33 |
| RBragg [%] | 2.93 | 1.43 |