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

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**Abstract**

*In situ* X-ray absorption and emission spectroscopies (XAS and XES) are used to provide details regarding the role of the accessibility and extent of redox activity of the Mn ions in determining the oxygen reduction activity of LaMnO3 and CaMnO3, with the XANES providing the average oxidation state, the EXAFS the local coordination environment, and the XES the population ratios of the Mn2+, Mn3+, and Mn4+ sites as a function of the applied potential. For LaMnO3 the XANES and XES show that Mn3+ is formed, but Mn4+ ions are retained, which leads to the 4*e-* reduction between 0.85 and 0.6 V. At more negative potentials, down to 0.2 V, EXAFS confirms an increase in oxygen vacancies as evidenced by changes in the Mn-O coordination distance and number, whilst the XES shows that the Mn3+ to Mn4+ ratio increases. For CaMnO3 the XANES and XES show formation of both Mn3+ and Mn2+ as the potential is made more negative, with little retention of Mn4+ at 0.2 V. The EXAFS for CaMnO3 also indicates the formation of oxygen vacancies, but in contrast to LaMnO3 this is accompanied by loss of the perovskite structure leading to structural collapse. The results presented have implications in terms of understanding of both the pseudocapacitive response of Mn oxide electrocatalysts and the processes behind degradation of the activity of the materials.

**TOC graphics**



**KEYWORDS:** perovskite oxides, oxygen reduction reaction, X-ray absorption/emission, LaMnO3, CaMnO3, Manganese Redox

**INTRODUCTION**

The increased interest in electrochemical energy storage/conversion systems such as metal-air batteries, fuel cells and electrolyzers arising from the interest in electrification of energy supply and distribution has motivated many studies of oxygen reduction and evolution (ORR and OER) electrocatalysts.[1-2](#_ENREF_1) The development of more efficient and stable materials are a critical step for the final introduction of these devices in the market. Platinum-based catalysts and IrO2 remain as benchmark materials for the ORR and OER, respectively, in acidic and alkaline environments,[3-4](#_ENREF_3) but significant efforts have also been focused on earth-abundant and low-cost materials.[5-6](#_ENREF_5) A growing number of publications on the electrocatalytic properties of Co, Ni, and Mn containing spinel and perovskite oxides have emerged in recent years.[7-8](#_ENREF_7) The mixed valency of individual elements in the parent materials, further complicated under operating conditions, make the identification of composition-activity relationships more difficult for such materials.[9](#_ENREF_9) A deeper understanding of the contributions of each component ion to the activity is required to more fully develop such relationships and enable the design of more active/stable electrocatalysts. [9-10](#_ENREF_9)

Mn based oxides are among the most active catalysts towards the oxygen reduction reaction (ORR) in alkaline solutions. After the seminal work by Bockris and Otagawa,[11](#_ENREF_11) and the elegant work of Suntivich *et al.* on perovskite oxides,[12](#_ENREF_12) the prevailing view is that a single electron occupancy of the eg orbital of the metal at the B-site of the perovskite structure represents the optimum configuration for oxygen electrocatalysis. This trend implies that LaMnO3+δ (eg~1) should be more active than CaMnO3 (eg~0), suggesting that there is an optimal oxidation state of the active metal. However, numerous works have shown that the orbital occupancy on Mn states changes in the potential range relevant to ORR. For example, our recent works on perovskite nanoparticles demonstrated that changes in the redox state of the B-site at Mn based perovskites are directly linked to their activity towards ORR.[13-14](#_ENREF_13) Studies on thin films have provided evidence that Mn3+ or a mixed valence Mn3+/Mn4+ corresponds to the active material.[15-18](#_ENREF_15) Ryabova *et al*. proposed that the formal potential of the Mn4+/Mn3+ redox transition could be used as a descriptor for the ORR activity,[19](#_ENREF_19) with the highest activity corresponding to the catalyst with the more positive redox potential.

Understanding the ORR mechanism at such complex materials requires direct information regarding the changes in the orbital occupancy of the Mn sites that can only be achieved using *in situ* characterization techniques. *In situ* XANES studies enable identification of the oxidation states of the metal atoms, whilst the EXAFS data enable study of the accompanying change in oxygen coordination. For example, Gorlin *et al.*[*20*](#_ENREF_20) and Risch *et al.*[*21*](#_ENREF_21) concluded that manganese was reduced below Mn3+ and contained significant fractions of Mn2+ by looking at the Mn K-edge and Mn L-edge, respectively, in agreement with previous studies by Lima *et al*. at the Mn K-edge.[22](#_ENREF_22) Although such X-ray absorption measurements provide element specific information, they only enable identification of the average oxidation state of the absorbing atom owing to the energy resolution of the spectra.

The resolution of the XANES can be improved by use of a High Energy Resolution Fluorescence Detection (HERFD) spectrometer, which enhances the pre-edge features and detail at the edge by overcoming the core-hole lifetime broadening of the 1s hole present in conventional K-edge XANES.[23-25](#_ENREF_23) The fractional contributions of the valence states to the average oxidation state can be obtained by analysis of the X-ray emission spectra (XES) and in particular the K*β* emission lines (3p → 1s), comprising the main K*β*1,3 and the K*β’* satellite peaks which are sensitive to the 3d spin state of the emitting atom.[26](#_ENREF_26) Traulsen *et al*. employed these methods to study the polarization induced changes to the oxidation state of Mn for a La0.5Sr0.5MnO3+δ solid-oxide fuel cell electrocatalyst under *operando* conditions at 500 °C, demonstrating that the average Mn oxidation state decreased from +3.4 at open circuit to +3.2, corresponding to 34% Mn4+, 49% Mn3+, and 17% Mn2+, at -800 mV applied potential.[27](#_ENREF_27) Here, we implement electrochemical in-situ XES and EXAFS to unravel the complex correlation between orbital occupancy of Mn sites and their electrocatalytic activities towards ORR. For the first time, we demonstrate that electrochemical signatures associated with LaMnO3 at potential close to ORR formal potential are linked to an increase in the orbital occupancy of Mn 3d sites as well as changes in the Mn-O bond distance and coordination numbers. XES enables visualization of the changes in oxidation states in terms of population ratio of Mn3+ (d4) and Mn4+ (d3) states. These changes are observed at significantly more negative potential in the case of CaMnO3, which is consistent with their lower activity towards the 4e- ORR. Furthermore, we also observe that the structural integrity of CaMnO3 is significantly more compromised upon potential cycling in comparison to LaMnO3.

**Results**

**Electrocatalytic behaviour of (La, Ca)MnO3 oxides.** Figure 1 shows the electrochemical response of LaMnO3 and CaMnO3 in Ar-saturated (a) and O2-saturated (b) 0.1 M KOH solution at 0.010 V s-1 for electrodes with the same mass of the oxides loaded on to the glassy carbon of a rotating disc electrode. The voltammogram (Figure 1a) of LaMnO3 in Ar-saturated electrolyte features two cathodic reduction peaks, which have previously been attributed to the formation of a partially reduced state, followed by reduction to Mn2+.[28-31](#_ENREF_28) The corresponding voltammogram of CaMnO3 is characterised by a broad reduction peak centred at 0.80 V vs. RHE (Reversible Hydrogen Electrode, against which all potentials in this manuscript are reported) previously ascribed to the reduction of Mn4+ to Mn2+.[30-31](#_ENREF_30) A small feature at ∼0.5 V superimposed on the main broad voltammetric peak is also observed, which may suggest the presence of Mn3+ sites. An increase in current, and thus in the charge involved in redox processes is observed for CaMnO3 compared to that for LaMnO3, indicating that a larger number of Mn atoms change oxidation state or that the change in oxidation state for those Mn atoms that are active is larger within the potential window under study.

Figure 1b shows the disk (*i*DISK, bottom panel) and ring (*i*RING, top panel) currents obtained at 1600 rpm and 0.010 V s-1 in an O2-saturated 0.1 M KOH solution for LaMnO3 and CaMnO3 in comparison with an electrode just containing Vulcan carbon. The ORR onset potential is significantly more positive than that for the Vulcan support (ca. 0.7 V, see black curve in figure 1), confirming that the reaction at potentials greater than 0.7 V takes place at the oxide particles. LaMnO3 presents the most positive onset potential, while CaMnO3 requires a higher overpotential to initiate the reaction. Substantial peroxide detection at the ring electrode, is only observed at potentials more negative than 0.7 V, indicating that the Vulcan carbon may contribute to the partial reduction of O2 to peroxide. However, as differences are observed between the LaMnO3 and CaMnO3 catalysts at potentials below 0.7 V, the 4 *e-* reduction is still taking place on the oxide. The calculated peroxide yields are provided as function of the electrode potential are provided in Figure S1. Comparing Figures 1a and 1b, we note that it is not until the first redox process occurs, that the electrodes start generating peroxide.



**Figure 1.** (a) Cyclic voltammograms of the LaMnO3 and CaMnO3 nanoparticles in Ar-saturated 0.1 M KOH solution at 0.010 V s-1. (b) Rotating ring-disk electrode (RRDE) responses at 1600 rpm in O2-saturated 0.1 M KOH at 0.010 V s-1. The Pt ring was held at a constant potential of 1.10 V. Oxide nanoparticles were supported on a Vulcan layer (50 µg cm-2) with a total oxide content of 250 µg cm-2. Data for the carbon electrode was 50 µg cm-2.

***In situ* XAS and XES studies.** *In situ* XAS spectra were collected in standard fluorescence mode using the SAMBA beamline at SOLEIL whilst applying potentials relevant to ORR, from 1.4 V to 0.2 V vs RHE in N2 purged 0.1 M KOH. Figure 2 shows the XANES spectra of the LaMnO3 (a) and CaMnO3 (b) catalysts. For LaMnO3 at 0.2 V, the edge position (determined at the half of the edge step) is shifted to lower energy by 1.2 eV relative to the spectrum at the starting potential (1.4 V); whereas for CaMnO3 at 0.2 V the edge is shifted by 6.7 eV towards lower energy compared to the starting potential. This difference is greater than the 4 eV observed between MnO2 and Mn2O3 standards (Fig. S2), corresponding to the Mn4+ and Mn3+ oxidation states, respectively. It is interesting to notice that for CaMnO3, the position of the maximum of the white line (defined as the maximum of the rising edge) also changes at 0.2 V compared to that at 1.4 V. The average Mn oxidation state can be estimated from the edge position by reference to a calibration plot generated from the reference samples as shown in Fig. S3. The oxidation state of the LaMnO3 sample determined in this manner does not show much variation with potential, +3.7 at 1.4 V going to +3.1 at 0.2 V, whilst that of CaMnO3 shows a much more significant shift from +4.7 at 1.4 V to +2.6 at 0.2 V. However, this method is rather approximate and can yield misleading results as the edge features of Mn are also dependent on the geometry and ligand environment.[32-33](#_ENREF_32" \o "Ignatov, 2001 #222) The average Mn oxidation state or number of unoccupied 3d states is more frequently probed by examination of the position of the pre-edge peak (1s → 3d) in the XANES (Figs. 3c and d) following the approach by Croft *et al.*[34](#_ENREF_34) The broadening and low intensity of the pre-edge features in the spectra obtained under *in situ* conditions, prevents a reliable analysis of the changes in oxidation state from these conventionally collected XANES data. Nevertheless, very little change in the position of the pre-edge peak was observed for the LaMnO3 indicating only a small decrease in the average Mn oxidation state, whilst a more significant change is observed for the CaMnO3 electrode.



**Figure 2.** XANES spectra (a) and (b) and the corresponding pre-edge regions (c) and (d) of the spectra at the Mn K edge for LaMnO3 (a) and (c) and CaMnO3 (b) and (d) perovskite electrodes recorded at different applied potentials. Data collected in N2 purged 0.1 M KOH.

Figures 3a and b show the comparison between the Fourier transforms (FTs) of the EXAFS data at different potentials for LaMnO3 and CaMnO3. LaMnO3 shows a decrease of amplitude for the first shell, and a slight compression of the Mn–O bond at 0.2 V. In the case of CaMnO3, the change with potential is much more pronounced with an expansion of the first peak to 1.8 Å and a contraction of the second shell to 2.9 Å at 0.2 V; revealing that the coordination sphere of Mn and thus the (crystal) structure changes with the applied potential. Whereas the EXAFS of the CaMnO3 dry electrode and immersed electrode at the starting potential of 1.4 V can still be fitted using the same structure as for the *ex situ* pellet (pellet spectra and fits provided in Fig. S4 and Table S1; that for the dry electrodes in Fig. S5 and Table S2; and at 1.4 V in Fig. S6 and Table S3), a decrease in the amplitude of the first peak in the Fourier transforms corresponding to Mn–O coordination is observed as the potential is made more negative (Fig. S7 and Table S4), which is attributed to the creation of oxygen vacancies. For the LaMnO3 the higher-shell structure of the perovskite is retained upon formation of oxygen vacancies as evidenced by the peaks in the Fourier transforms at *R* ≥ 2 å. In contrast, for CaMnO3 the Fourier transform and thus, structure, is significantly different at 0.2 V.

A close up of a map

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**Figure 3.** Fourier transforms of the k3-weighted Mn K-edge EXAFS of LaMnO3 (a) and CaMnO3 (b) at different potentials. The EXAFS data and fits for the first coordination shell in both *k-* and *R*-space are shown in Fig. S7 and Table S4. Data recorded in N2 purged 0.1 M KOH at room temperature. 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.

High Energy Resolution Fluorescence Detected XANES (HERFD-XANES) enhances features present in the near edge region of the absorption spectrum.[23-25](#_ENREF_23) *In situ* HERFD data and Kβ XES spectra were collected on the I20 Scanning beamline at the Diamond Light Source using a point-point Rowland circle XES spectrometer. Figures 4a and b compare the Mn K-edge HERFD-XANES as a function of potential for LaMnO3 and CaMnO3, respectively (data for the reference materials is shown in Figure S8). For LaMnO3 (Fig. 5a), decreasing the potential results in the reduction of Mn as indicated by the shift of the edge position and white line to lower energy, in agreement with the conventional XANES data described above. Two peaks in the pre-edge region arising from t2g and eg orbitals are identified as A1 (low energy) and A2 (high energy) are observed (Fig 5c). Both peaks slightly shift towards lower energies, with the A2 peak decreasing in intensity more significantly as the potential is made more negative. For CaMnO3 (Fig 5b), stepping the potential to more negative values results in a more dramatic shift in the Mn edge position by ~6 eV towards lower energy. The pre-edge region (Fig. 5d) is characterised by a single more intense peak with a low energy shoulder at 1.4 and 0.5 V, with only the A1 peak clearly observed at 0.2 V. As in the case of the conventional XANES spectra, the complex dependency of the pre-edge features on geometry and ligand environment makes further identification of the relative fractions of the Mn species by linear combination fitting to the limited HERFD-XANES reference sample spectra collected inappropriate. However, these data do suggest a stronger potential dependence of the valency and coordination environment of Mn for CaMnO3 than for LaMnO3 in agreement with the conventional XAS data.



**Figure 4.** HERFD-XANES spectra (a) and (b) and the corresponding pre-edge regions (c) and (d) obtained at the maximum of the Kβ1,3 line of LaMnO3 (a) and (c) and CaMnO3 (b) and (d) as a function of the applied potential. Data recorded in N2 purged 0.1 M KOH at room temperature.

Further details of the Mn valency can be obtained by analysis of the X-ray emission spectra (XES), taking advantage of the spin, oxidation state and ligand sensitivity of the Mn K*β* lines.[35-36](#_ENREF_35) Figure 5 compares the Mn K*β* XES of LaMnO3 (a) and CaMnO3 (b) as a function of the applied potential. The spectra feature a strong K*β*1,3 peak and a broad K*β*’ shoulder at lower emitted energies due to different 3d spin-states.[26](#_ENREF_26) Upon changing the potential from 1.4 V to 0.2 V, the Mn valence decrease is reflected in the shift of the K*β*1,3 maximum to higher energy and accompanied by intensity changes in the K*β*’ region. When comparing the spectra with those collected for the reference samples (Fig. S9), the *in situ* spectra collected for LaMnO3 lie in between those for the Mn4+ and Mn3+ references; whereas in the case of CaMnO3 the spectra lie in between those for Mn4+ and Mn2+.



**Figure 5.** Normalised Mn Kβ XES spectra measured at 100 eV from the absorption edge for LaMnO3 (a) and CaMnO3 (b) at different applied potentials. Linear combination of the normalized Mn Kβ XES spectra for LaMnO3 (c) and CaMnO3 (d) for the electrodes inside the cell but without any applied potential (OCP). Percentage of the different cation species for LaMnO3 (e) and CaMnO3 (f) at the different potentials under study obtained by linear combination fitting of the XES data.

Previous XES studies have shown that such spectra can be fitted as a linear combination of the K*β* of the constituent cation species.[37-42](#_ENREF_37) The normalised Mn-K*β* spectra for the reference samples (Figure S9) collected in this study were thus linearly combined to fit the Mn-K*β* spectra for LaMnO3 and CaMnO3. Figures 5c and d show the normalized Mn K*β* spectra for the LaMnO3 and CaMnO3 electrodes at the open circuit potential (OCP, corresponding to 1.9 V) as a combination of the reference standards (fits for the different potentials can be found in Fig. S10 and Table D5, as well as statistics of the fits in Table S6). The results yield an average oxidation state of +3.4 for LaMnO3 and +4.1 for CaMnO3 at OCP with the relative fractions of the Mn2+, Mn3+, and Mn4+ species shown in Figs. 5e and f. Application of 1.4 V results in an increase in the Mn4+ and decrease in the Mn3+ percentage for LaMnO3 and a correspondingly, but smaller change for CaMnO3. Decreasing the potential to 0.5 V and then 0.2 V results in conversion of the Mn4+ ions to Mn3+ for LaMnO3, with little change in the percentage of Mn2+. In contrast the Mn4+ ions are observed to be converted to both Mn3+ and Mn2+ for the CaMnO3 electrode. As evidenced by the EXAFS data presented above (Fig. 4), the perovskite structure is not retained at 0.2 V for CaMnO3. Further evidence of this structural change was observed in the *ex situ* XRD obtained on the dried electrodes after the XES and HERFD-XANES measurements in Fig. S11. We propose that it is this over reduction and increase in the fraction of Mn2+ that results in the structural changes accompanying the formation of oxygen vacancies.

The implications of the trends in figures 5e-f are crucially important in correlating the intrinsic electrochemical responses of the perovskites and their electrocatalytic activity towards the ORR. As shown in Figure 1, the pseudo-capacitive responses in the LaMnO3 voltammetric profile coincide with significant changes in XES, confirming that Mn 3d states are being populated/depopulated across the potential range in which the ORR is taking place. On the other hand, the relatively weak changes in the XES features observed in CaMnO3 across the same potential range suggest that only a fraction of the large pseudocapacitive responses is linked to Mn 3d states. It is not entirely clear which orbitals contribute to the density of states responsible for the pseudo-capacitive responses in CaMnO3, although electronic structure calculations by Molinari et al. have shown a sizeable density of O 2p states within the band gap of partially reduced CaMnO3.[43](#_ENREF_43)

The tolerance of the catalysts to repeated cycles 1000 times to simulate an accelerated stress test (AST) was further investigated using conventional XAS and XRD (experimental details of AST can be found in the Methods Section, and cyclic voltammograms recorded before and after the AST are presented in Fig. S12). Figure 6 shows the *ex situ* XANES and Fourier transforms of the EXAFS data collected before and after the AST (fits to the EXAFS data are presented in Figure S13 and fitting parameters in Table S7, with the XRD data shown in Fig S14). All datasets confirm the results from the *in situ* XAS measurements presented above, with the LaMnO3 undergoing very little structural change, whilst the perovskite structure is significantly degraded for the CaMnO3 electrocatalyst. In the case of LaMnO3 it can be observed that the perovskite structure is maintained after the AST, with only a slight expansion of the Mn–La distance. In the case of CaMnO3, the perovskite structure is no longer observed after the AST, and the Mn–O coordination has changed to a tetrahedral (instead of an octahedral). Although the full structure is still unknown, it is highly likely this is a mixture of different phases. Literature studies on MnOx thin films exposed to an ORR-relevant potential of 0.7 V vs RHE showed the production of a disordered Mn3II,III,IIIO4 phase.[20](#_ENREF_20)



**Figure 6.** XANES spectra (a) and (b) and the corresponding Fourier transforms of the k3-weighted EXAFS (c) and (d) of the spectra at the Mn K edge for LaMnO3 (a) and (c) and CaMnO3 (b) and (d) perovskite electrodes recorded at before and after the accelerated stress test.

**Discussion**

Our data show that the pseudo-capacitive responses observed in the voltammograms (Figure 1a) are associated with changes of the electron population of Mn 3d states in LaMnO3 which are manifest at the ORR onset potential (Figure 1b). On the other hand, changes in the redox states of Mn sites are observed at a more negative potentials in CaMnO3, despite of a significant pseudo-capacitive current, which is consistent with the lower activity towards the ORR. Whilst the *in situ* XANES and HERFD-XANES correspond to a greater fraction of Mn3+ for LaMnO3 than for CaMnO3 over the potential range for which ORR is observed, further details were obtained from the XES (Figure 5). For LaMnO3 these measurements showed that Mn4+ was found to persist throughout the potential range over which the RRDE measurements were conducted, wherein less of the 2*e-* ORR product was observed at the ring than was found for CaMnO3. In contrast, the XES data of CaMnO3 showed that the fraction of Mn4+ states significantly decreases at potentials more negative than 0.6 V vs RHE. Furthermore, the EXAFS data show that whilst the Mn-O distance for LaMnO3 was found to be stable (or even contracting a little) over the potential range, that for CaMnO3 increased as the potential was made more negative. Such an expansion favours side-on adsorption of O2,[17](#_ENREF_17) and this agrees with the increased fraction of hydroperoxide formed compared to the LaMnO3.

There has been some suggestions in the literature that oxygen vacancies may participate in the ORR by turning on the bidentate adsorption of O2,[44](#_ENREF_44) stabilising the HO2- species, which thus yields more of the 4*e-* reduction products. For both LaMnO3 and CaMnO3 reduction of the Mn ions was found to be accompanied by the formation of oxygen vacancies as evidenced in the EXAFS, evidenced as a decrease in Mn–O coordination number. The EXAFS results shown in our study suggest that LaMnO3 is better able to tolerate the formation of these vacancies. In contrast, the EXAFS data suggest CaMnO3 is not able to tolerate the formation of oxygen vacancies with the perovskite structure being lost, presumably due to the formation of Mn2+ ions and correspondingly greater oxygen loss, which then contributes to the structural collapse of CaMnO3 observed following accelerated stress testing.

The results presented above demonstrate the added information that may be obtained from a combined approach of *ex situ* and *in situ* X-ray characterisation of such electrocatalysts and, in particular, the use of XES to provide details of the relative populations of the various oxidation states, compared to the average oxidation state provided by XANES measurements. The combined use of these techniques has enabled a deeper understanding of the processes observed as the pseudocapacitive response in the voltammetry of these Mn oxides and highlighted the importance of the Mn4+/3+redox couple in achieving the full 4*e*- reduction of oxygen.

**Methods section**

**Sample preparation.** (La, Ca)MnO3 perovskite nanoparticles were synthesized employing an ionic liquid based route described in previous works.[13-14](#_ENREF_13), [29](#_ENREF_29) First, a dispersion of Mn(NO3)3 (0.5 mL, 0.1 M in H2O) and 0.5 mL of the corresponding A-site metal nitrate (0.5 mL, 0.1 M in H2O) in 1-ethyl-3-methylimidazolium acetate (1 mL) was prepared and kept under stirring conditions. After heating at 80 °C for 4 h to ensure all water was removed, cellulose (100 mg) was added and the mixture was stirred for 20 min. The gel-like mixture was calcined for 2 h at 700 °C for LaMnO3 and 850 °C for CaMnO3, to ensure single-phase formation.

**Materials characterization.** X-ray diffraction (XRD) patterns were recorded using a Bruker AXS D8 Advance diffractometer with a θ-θ configuration, using Cu Kα radiation (λ=0.154 nm). The XRD patterns were refined by the Rietveld method using the FULLPROF program.[45-46](#_ENREF_45) The following parameters were refined: scale factor, background coefficients, zero-point error and positional coordinates. The isotropic thermal factors for all the atoms were fixed to a standard value of 1 Å2. No cation deficiency was detected and so the occupancy factors for both LaMnO3 and CaMnO3 were fixed to 1. XRD patterns of the as-synthetised LaMnO3 and CaMnO3 oxide nanoparticles can be found in Fig. S15 and structural parameters obtained by Rietveld method in Table S8. Transmission electron microscopy (TEM) was obtained using a JEOL JEM-1400Plus and representative images for both materials are shown in Fig. S16.

**Rotating ring-disk electrochemical measurements.** A three-electrode cell was used to conduct the electrochemistry experiments, using a rotating ring-disk electrode (RRDE) fitted to an ALS rotation controller and connected to a CompactStat bipotentiostat (Ivium). The RRDE electrode consisted of a 4 mm glassy carbon disk surrounded by a Pt ring. The collection efficiency was experimentally determined to be 0.4. A graphite rod and a Hg/HgO (in 0.1 M NaOH) were used as counter and reference electrodes, respectively. Measurements were recorded in 0.1 M KOH solution saturated with either purified Ar or O2. The sample loading (per unit area of the glassy carbon disk) on the electrode surface was 250 µgOXIDE cm-2, 50 µgVULCAN cm-2, and 50 µgNAFION cm-2.

**Preparation of electrodes and in situ XAS and XES measurements.** Button electrodes were prepared by painting the catalyst ink onto a carbon paper support with a loading of 0.5 mg Mn cm-2.All measurements were collected in situ, using our custom designed electrochemical cells[47](#_ENREF_47) connected to an Autolab PGSTAT101 potentiostat. Measurements were collected in N2 purged 0.1 M KOH electrolyte.

Extended X-ray Absorption Fine Structure (EXAFS) measurements were carried out at room temperature at the SAMBA beamline of Soleil Synchrotron (Saclay, France).[48](#_ENREF_48) The beamline is equipped with a sagittally focusing Si 220 monochromator and two Pd-coated collimating/focusing mirrors to remove higher harmonics. Calibration of the monochromator was carried out using a Mn foil, and XAFS spectra were recorded in fluorescence mode at the Mn K-edge (6539 eV) using a Canberra 35-elements monolithic planar Ge pixel array detector. The spectra were aligned using the Mn foil response. The data was analysed using the Athena and Artemis softwares.[49](#_ENREF_49)

X-ray emission spectroscopy (XES) and High Energy Resolution Fluorescence Detected (HERFD-XANES) measurements were conducted at Beamline I20-Scanning, of Diamond Light Source,[50-51](#_ENREF_50) operating with a ring energy of 3 GeV and at a current of 300 mA. The beamline is equipped with an in-house designed four-bounce scanning Si(111) monochromator, and the harmonic rejection was achieved by using two Si-coated mirrors. An X-ray emission spectrometer based on a 1 m diameter Rowland circle operating in the Johann configuration in the vertical plane with three spherically-bent Ge(440) analyzers to collect the emission signal was used for the experiment (see Figure S17).[52](#_ENREF_52) The XES spectra have been normalized with respect to their total area using the range 6465-6497 eV. All the HERFD-XANES measurements were collected at the peak of Kβ1,3 line and non-resonant XES spectra were measured 100 eV above the absorption edge of Mn.

**Accelerated stress test (AST) cycling**

Studies on the stability of the proposed materials was carried out by performing accelerated stress tests, where the potential was cycled between 1.1 and 0.6 V vs RHE at 0.050 V s-1, during 1000 cycles; following the DOE standard procedures.

**Notes**

The authors declare no competing interests.

Data are available at the University of Southampton data repository,  <https://doi.org/10.5258/SOTON/D1810>

**ASSOCIATED CONTENT**

**Supporting Information.**

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**Figure S1.** Percentage of peroxide formation during ORR. **Figure S2.** Mn XANES of references. **Figure S3.** Calibration plot for the determination of the average Mn oxidation state from the edge positions. **Figure S4.** Mn K-edge XANES and *k3* weighted χ and *k3* weighted Fourier transform EXAFS data and fits for the pellets. **Figure S5.** *k3* weighted χ data and *k3* weighted Fourier transform EXAFS data and fits for the dry electrodes. **Figure S6.** *k3* weighted χ data and *k3* weighted Fourier transform EXAFS data and fits for the data collected at 1.4 V. **Figure S7.** *k3* weighted χ and *k3* weighted Fourier transform EXAFS data and first shell fits for the data collected at at different potentials. **Figure S8.** HERFD-XANES spectra at the Kβ1,3 line of the reference compounds. **Figure S9.** Mn Kβ XES spectra of references. **Figure S10.** Linear combination fits of the Mn Kβ XES spectra of the data collected at different potentials. **Figure S11.** Ex situ X-ray powder diffraction measured before and after electrochemistry. **Figure S12.** Cyclic voltammograms of the LaMnO3 and CaMnO3 electrodes before and after the AST. **Figure S13.** *k3* weighted χ data and *k3* weighted Fourier transform EXAFS data and fits for the data collected after AST. **Figure S14.** Ex situ X-ray powder diffraction measured before and after AST. **Figure S15.** XRD patterns of as-synthesized oxides. **Figure S16.** Representative TEM of synthesised oxide nanoparticles. **Figure S17.** Schematic view of the I20-scanning branch of Diamond Light Source.

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**Author contributions.**

V.C. and A.E.R. conceived the experiments. V.C. synthetised the materials and performed the electrochemistry experiments. V.C. and D.J.F. analysed the electrochemical data. EXAFS data was collected by V.C., A.S.L. and D.I.. XES and HERFD-XANES data were collected by S.H., A.F., V.C., A.S.L., H.H. and A.E.R.. EXAFS, XES and HERFD-XANES data analyses were performed by V.C. and A.E.R. All authors contributed to the analysis of the results, discussion, writing and revision of the manuscript. All authors have given approval to the final version of the manuscript.

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