Synthesis and characterisation of oxyanion-doped manganites for potential application as SOFC cathodes

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TOC: Oxyanion doping shows beneficial effects on both the conductivity of CaMnO$_3$ as well as its performance as a SOFC cathode. At 800ºC, the values obtained for 5% doping of B and P were 0.37 and 0.30 Ω·cm$^2$ respectively. These results entail a significant improvement with respect to the undoped compound (CaMnO$_3$), 1.50 Ω·cm$^2$ at 800ºC.
Abstract

In this paper we report the successful incorporation of borate and phosphate into CaMnO$_3$ and borate into La$_{1-y}$Sr$_y$MnO$_3$$_{3-\delta}$. For CaMnO$_3$, an increase in the electronic conductivity was observed, which can be correlated with electron doping due to the oxyanion doping favoring the introduction of oxide ion vacancies (as well as the higher valence of P$^{5+}$ compared to Mn$^{4+}$ in the case of phosphate doping). The highest conductivity at 800ºC was observed for CaMn$_{0.95}$P$_{0.05}$O$_{3-\delta}$, 43.0 S·cm$^{-1}$, in comparison with 7.6 S·cm$^{-1}$ for undoped CaMnO$_3$ at the same temperature. For La$_{1-y}$Sr$_y$MnO$_3$$_{3-\delta}$ the conductivity suffers a decrease for all compositions on borate doping, attributed to a reduction in the hole (Mn$^{4+}$) concentration. In order to investigate the potential of these materials as SOFC cathodes, the chemical compatibility with Gd$_{0.1}$Ce$_{0.9}$O$_{1.95}$ (CGO10) has also been investigated. For the calcium manganites, the lowest temperature examined without reaction was 900 ºC, with minor amounts of Ca$_4$Mn$_3$O$_{10}$ observed at 1000ºC. Composites of these cathode materials with 50% CGO10 were examined on dense CGO10 pellets and the area specific resistances (ASR) in symmetrical cells were determined. The ASR values, at 800ºC, were 1.50, 0.37 and 0.30 Ω·cm$^2$ for CaMnO$_3$, CaMn$_{0.95}$B$_{0.05}$O$_{3-\delta}$ and CaMn$_{0.95}$P$_{0.05}$O$_{3-\delta}$, respectively. For the lanthanum strontium manganites, the B-doped compositions showed an improvement in the ASR values with respect to the parent compounds, despite the lower electronic conductivity. This may be due to an increase in ionic conductivity due to borate incorporation leading to the formation of oxide ion vacancies. Thus these preliminary results show that oxyanion doping has a beneficial effect on the performance of perovskite manganite cathode materials, and suggests that this doping strategy warrants further investigation in other perovskite cathode systems.
Keywords: SOFC, cathode, oxyanion doping, manganite
1. Introduction

Perovskite manganites have attracted considerable interest due to potential applications as cathode materials in the field of Solid Oxide Fuel Cells (SOFCs). Traditionally doping strategies for such materials has focused on substitution with cations of similar size, e.g. Sr for La [1-5]. In this study we investigate an alternative strategy, the incorporation of oxyanions (borate and phosphate). The approach employed stems from prior observations on the incorporation of oxyanions into perovskite-type cuprate superconductors and related phases [6-13]. This work demonstrated that the perovskite structure can incorporate significant levels of oxyanions (carbonate, borate, nitrate, sulfate, phosphate).

More recently we have illustrated the potential of doping strategies related to the incorporation of tetrahedral oxyanions such as sulphate, phosphate, and silicate. In particular, we have shown that the partial substitution of these oxyanions at the In/Sc site in Ba$_2$(In/Sc)$_2$O$_5$ leads to the introduction of disorder on the oxygen sublattice and a corresponding enhancement in the low temperature ionic conductivity [14-18]. In terms of electronic conducting materials, we have also reported the successful incorporation of silicate, phosphate and sulphate into SrMO$_3$ (M = Co, Mn), leading to a large enhancement in the electronic conductivity [19, 20]. In these latter examples, this large enhancement in the conductivity could be explained by a change from a 2H- perovskite (containing face sharing of octahedra) to a 3C- perovskite (containing corner sharing of octahedra). In this paper we extend our oxyanion doping work to examine the potential incorporation of borate, phosphate into two manganite systems, CaMnO$_3$ and La$_{1-y}$Sr$_y$MnO$_{3-δ}$. In these cases, no change in packing arrangement would be expected, as the
parent phases already contain corner linked octahedra. We report the effect of this doping on the structural and electrical properties to examine the potential for SOFC applications.

2. Experimental

La$_2$O$_3$ (Aldrich, 99.99%), SrCO$_3$ (Aldrich, 99.9%), CaCO$_3$ (Aldrich, 99%), MnO$_2$ (Aldrich, 99%), H$_3$BO$_3$ (Aldrich, 99.5%) and (NH$_4$)H$_2$PO$_4$ (Aldrich, 98%) were used to prepare CaMn$_{1-x}$M$_x$O$_{3-\delta}$ (M=B and P, $x \leq 0.10$) and La$_{1-y}$Sr$_y$Mn$_{1-x}$M$_x$O$_{3-\delta}$ (M=B and P; $y=0.3$, $0.4$ and $0.5$; $x \leq 0.10$) samples. For CaMn$_{1-x}$M$_x$O$_{3-\delta}$ the powders were intimately ground and heated initially to 1100°C for B-doping and 1200°C for P-doping for 12h. They were then ball-milled (350 rpm for 1 hour, Fritsch Pulverisette 7 Planetary Mill) and reheated to 1200°C for B-doping and 1250°C for P-doping for a further 12h. This step was repeated two times for both series. For La$_{1-y}$Sr$_y$Mn$_{1-x}$M$_x$O$_{3-\delta}$, the powders were intimately ground and heated initially at 1100°C for 12h. They were then ball-milled (350 rpm for 1 hour) and reheated at 1200°C for a further 12h. A final heat treatment at 1300°C for a further 12h was then employed.

Powder X-ray diffraction (XRD) (Bruker D8 diffractometer with Cu K$_{\alpha 1}$ radiation) was used to demonstrate phase purity, as well as for cell parameters determination. For the latter, the GSAS suite of programs was used [21].

Since B could be incorporated either as BO$_3$$^{3-}$ or BO$_4$$^{5-}$, low field (2.35 T) solid state $^{11}$B MAS NMR measurements were performed at ambient temperature in an attempt to determine the B coordination in the CaMnO$_3$ samples. The data were collected on a Chemagnetics CMX-100 spectrometer operating at a characteristic $^{11}$B Lamor frequency of 32.08 MHz. All measurements were undertaken using a Bruker 2.5 mm probe which
accommodated MAS frequencies of 31.25 kHz. The data was acquired using a $\theta - \tau - 2\theta - \tau$ - acq solid echo experiment where $\tau$ delay was rotor synchronised with the MAS rate. Nutritional angles and pulse powers were calibrated using solid NaBH$_4$ with a ‘non-selective’ (or solution) $\pi/2$ pulse time of 5$\mu$s being obtained; from this calibration ‘selective’ $\theta/2\theta$ pulse times 1$\mu$s/2$\mu$s were employed in the solid echo experiment. All $^{11}$B chemical shifts are indirectly referenced against the primary IUPAC standard of BF$_3$.Et$_2$O (in CDCl$_3$) using the secondary solid standard of NaBH$_4$ (-42.16 ppm).

Oxygen contents were estimated from thermogravimetric analysis (Netzsch STA 449 F1 Jupiter Thermal Analyser). Samples were heated at 10$^\circ$C/min to 1200$^\circ$C in N$_2$ and held for 30 minutes to reduce the Mn oxidation state to 3+, with the original oxygen content and average Mn oxidation state then being determined from the mass loss observed. Pellets for conductivity measurements were prepared as follows: the powders were first ball-milled (350 rpm for 1 hour), before pressing as pellets and sintering at 1200$^\circ$C (M=B) and 1250$^\circ$C (M=P) for 12h for calcium manganites, and at 1300$^\circ$C for 12h for the lanthanum strontium manganites. Conductivities were then measured using the four probe dc method. Four Pt electrodes were attached with Pt paste, and then the sample was fired to 800$^\circ$C in air for 1 hour to ensure bonding to the sample. The samples were then furnace cooled to 350$^\circ$C in air and held at this temperature for 12 hours to ensure full oxygenation.

The chemical compatibility of the oxyanion-doped materials with Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (CGO10) (Sigma-Aldrich) was evaluated by XRD. Powder mixtures of electrolyte and electrodes (1:1 wt.%.) were calcined between room temperature (RT) and 1100$^\circ$C for 24h and then analyzed by XRD to determine if any reaction had occurred.
To elucidate the potential of these materials as SOFC cathodes, symmetrical electrodes were coated on both sides of dense CGO10 pellets (sintered at 1500°C for 12h) using a suspension prepared with a mixture of electrolyte and electrodes (1:1 wt%) and DecofluxTM (WB41, Zschimmer and Schwarz) as binder material. For CaMn1-xMxO3-δ the symmetrical cells were fired at 900 and 1000°C, and for La1-ySryMn1-xMxO3-δ at 1000 and 1100 ºC for 1 h in air. Afterwards, a Pt-based ink was applied onto the electrodes to obtain a current collector layer and finally fired at 800 ºC for 1 hour. Area-specific resistance (ASR) values were then obtained under symmetrical air atmosphere in a two electrode configuration. Impedance spectra of the electrochemical cells were collected using a HP4912A frequency analyser, at open circuit voltage (OCV), in the 5 Hz - 13 MHz frequency range with ac signal amplitude of 100 mV. The spectra were fitted to equivalent circuits using the ZView software [22], which allows an estimation of the resistance and capacitance associated with the different cell contributions.

3. Results and discussion

Solid solution range

\( \text{CaMn}_{1-x}M_xO_{3-\delta} \) (\( M = B, P \))

For \( \text{CaMn}_{1-x}M_xO_{3-\delta} \) (\( M = B, P \)), X-ray diffraction data showed the successful incorporation of up to 5% B, P (\( x = 0.05 \)) with no change in cell symmetry on doping. Higher dopant amounts led to the segregation of secondary phases, such as \( \text{Ca}_3\text{B}_2\text{O}_6 \) (PDF 48-1885) (see Figure 1). Confirmation of the importance of borate/phosphate was shown by the fact that equivalent Mn deficient samples \( \text{CaMn}_{1-x}O_{3-\delta} \) (\( x = 0.05 \)) with no added borate/phosphate
gave the segregation of secondary phases, such as Ca$_4$Mn$_3$O$_{10}$ (PDF 089-5427) (Figure 1a).

Cell parameters were determined from the X-ray diffraction data using the Rietveld method (see Table 1). The change in cell parameters for these oxyanion doped perovskite materials is a balance between the effect of the smaller size of B$^{3+}$ and P$^{5+}$, which would be expected to lead to a reduction in cell volume, and the associated reduction of Mn$^{4+}$ to give a greater concentration of Mn$^{3+}$, which would be expected to lead to an increase in cell volume. The formation of 3+ species through these oxyanion doping strategies is predicted by the following defect equations:

\[
\begin{align*}
H_3BO_3 + 2Mn^{3+} + O_2 \rightarrow B^{3+} + Mn^{4+} + V_{O^-} + 1/2 O_2 + H_2O + MnO_2 \\
\text{(for BO}_4\text{)}^5 & \quad \text{[1]} \\
\text{or} \\
2H_3BO_3 + 6Mn^{3+} + 4O_2 \rightarrow 2B^{3+} + 4Mn^{4+} + 3V_{O^-} + 3/2 O_2 + 3H_2O + 2MnO_2 \\
\text{(for BO}_3\text{)}^3 & \quad \text{[2]} \\
NH_4H_2PO_4 + 4Mn^{3+} + O_2 \rightarrow P^{3+} + 3Mn^{4+} + V_{O^-} + 3/4 O_2 + NH_3 + 3/2H_2O + MnO_2 \\
\text{(for PO}_4\text{)}^3 & \quad \text{[3]}
\end{align*}
\]

As can be seen from the above equations, a key driving force for the reduction of Mn$^{4+}$ to Mn$^{3+}$ is the introduction of oxide ion vacancies due to the lower coordination (tetrahedral rather than octahedral) of the dopant. For the B-doped samples all cell volumes are slightly smaller than that of CaMnO$_3$ (Table 1). This decrease in comparison with the undoped compound is likely due to the small size of boron and to the low levels of Mn$^{3+}$ introduced. The oxygen contents and average Mn oxidation states were determined by TGA and these data supported the relatively low reduction in the Mn oxidation state in the B-doped samples (Table 3). For the P-doped samples all cell volumes are bigger than those of CaMnO$_3$ and the B-doped system, consistent with greater reduction of Mn$^{4+}$ in
this case, as indicated by the TGA data (Table 3). From the defect equations, the lower degree of reduction for the CaMn_{1-x}B_xO_{3-δ} samples would suggest incorporation of B as BO_4^{5-}. In order to try to confirm this, solid state \(^{11}\)B MAS NMR measurements were performed for CaMn_{0.95}B_{0.05}O_{3-δ} (data shown in Figure 2; NMR parameters used to simulate these data are summarized in Table 4). The acquired lineshape can be deconvoluted into three components represented by apparent centre-of-gravity shifts (δ); the dominant resonance at δ 152 ppm represents ~40% of the total B speciation, while the other highly shifted resonances are observed downfield at δ 481 ppm (~37% abundant) and upfield at δ -214 ppm (~23% abundant) from the central resonance. These shifts do not represent isotropic chemical shifts (δ\text{iso}) as they are uncorrected for second order quadrupolar contributions. Furthermore, these resonances will also experience a paramagnetic contribution to their observed shifts from the proximate Mn^{3+/4+} nucleus which is unaccounted for quantitatively in this analysis. These large reported \(^{11}\)B shifts are well outside the conventional shift range describing B speciation in ordered (crystalline) and amorphous (glass) oxo environments [23] and thus suggests that a significant contribution to their magnitude from the paramagnetism. Hence, the three predominant resonances observed can be ascribed to the relative position of the Mn^{3+/4+} ion in the coordination sphere of each B position as defined by the perovskite lattice. From previous MAS NMR studies on paramagnetic systems, the direction and magnitude of the induced paramagnetic shifts suggests that a significant contribution from a dipolar mechanism may characterize this phenomenon [24-27]. In addition, these paramagnetically shifted resonances also experience a line broadening phenomenon, as observed from linewidths shown in Figure 2. The deconvolution of this manifold of
resonances requires a large Gaussian broadening factor (typically 10 – 20 kHz, see Table 4) which effectively accommodates broadening generated by the positional disorder in the perovskite lattice, and the additional broadening contribution generated by the paramagnetic interaction with the Mn\(^{3+/4+}\) positions. From the centre-of-gravity of the resonance manifold it is expected that these resonances may represent four coordinate B positions in line with the predictions from the cell parameters data outlined above, although a component of this speciation (particularly the upfield component) may also represent a three coordinate species.

\(La_{1-x}Sr_xMn_{1-x}M_xO_3-\delta\) (\(M=B, P\))

For \(M=B\), the X-ray diffraction data showed the samples were successfully doped up to \(x=0.05\). Higher dopant amounts led to the segregation of secondary phases (see Figure 3). For \(M=P\), the X-ray diffraction data showed secondary phases (such as \(Sr_3La(PO_4)_3\), PDF 80-1597) at all levels of doping analysed. Therefore, these P-doped samples were not studied further. Confirmation of the importance of borate was shown by the fact that equivalent Mn deficient samples \(La_{1-y}Sr_yMn_{1-x}O_3-\delta\) with no added borate gave the segregation of secondary phases, such as \(LaMn_2O_5\) (PDF 088-0084) (Fig. 2a). Hereafter, all the results for the \(La_{1-y}Sr_xMn_{1-x}M_xO_3-\delta\) series focus on the \(M=B\) series.

The cell parameter determination showed no change in cell symmetry on doping. As described above for doping in CaMnO\(_3\), the change in cell parameters for these oxyanion doped perovskite materials is a balance between the effect of the smaller size of B\(^{3+}\) and the associated reduction of Mn\(^{4+}\) to give a greater concentration of Mn\(^{3+}\) (see defect eq. 1 and 2). The calculated cell volumes of the doped samples in this case were all slightly
bigger than those of the parent compounds (Table 2). This is most likely due to the effect of a reduction in the Mn\(^{4+}\) content. In line with this, the Mn oxidation state estimated from TGA measurements indicated only a small level of Mn\(^{4+}\); average Mn oxidation states were 3.07 for both La\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{0.95}\)B\(_{0.05}\)O\(_{3-\delta}\) and La\(_{0.6}\)Sr\(_{0.4}\)Mn\(_{0.95}\)B\(_{0.05}\)O\(_{3-\delta}\) (see Table 3).

**Conductivity measurements**

*CaMn\(_{1-x}\)M\(_x\)O\(_{3-\delta}\)*

The temperature dependencies of the conductivities of these phases are shown in figure 4. For CaMnO\(_3\), as expected, the data showed very low conductivities (1.9–7.6 S·cm\(^{-1}\) between 600–800 °C) due to the lack of significant mixed valency. For all doped samples a large improvement in the conductivity was observed. For the B-doped samples, enhanced conductivity values of 18–24 S·cm\(^{-1}\) were observed between 600–800 °C (table 3), which can be attributed to the introduction of Mn\(^{3+}\) as illustrated by the defect equations described earlier. P-doping gave the highest conductivity values in this study, reaching a maximum value at x=0.05 (43.0–52.8 S·cm\(^{-1}\) between 600–800 °C). The importance of borate/phosphate was confirmed through conductivity measurements on Mn deficient samples CaMn\(_{0.95}\)O\(_{3-\delta}\) with no added borate/phosphate, which gave low conductivity values (1.2–3.5 S·cm\(^{-1}\) between 600–800 °C), comparable to undoped CaMnO\(_3\).

For both borate and phosphate doping, higher levels, e.g. x=0.10 values, led to lower conductivities (not shown in Figure 4), likely due to the presence of impurities. The 5% B, P doped (x=0.05) samples were chosen for the cathode testing experiments.
La$_{1-y}$Sr$_y$Mn$_{1-x}$B$_x$O$_{3-\delta}$

Conductivity data for this series are shown in Figure 5. For the parent materials, the data show, at high temperature, the behavior described by Misuzaki et al. [28] for La$_{1-x}$Sr$_x$MnO$_3$ ($0 \leq x \leq 0.7$), where conductivity increases up to $x=0.5$. When the samples are doped with borate, the conductivity suffers a decrease for all compositions due to a reduction in Mn$^{4+}$ (hole) concentration (the oxidation states were determined to be 3.07 for La$_{0.7}$Sr$_{0.3}$Mn$_{0.95}$B$_{0.05}$O$_{3-\delta}$ and La$_{0.6}$Sr$_{0.4}$Mn$_{0.95}$B$_{0.05}$O$_{3-\delta}$, Table 3). While this would appear to be likely to be detrimental to fuel cell performance it is possible that the decrease in electronic conductivity may be partially compensated by an increase in ionic conductivity due to the formation of oxide vacancies, predicted by the incorporation of borate (Eq. 1 and 2). The samples were therefore still examined further for potential cathode applications. The compositions with the higher electronic conductivity, La$_{0.7}$Sr$_{0.3}$Mn$_{0.95}$B$_{0.05}$O$_{3-\delta}$ and La$_{0.6}$Sr$_{0.4}$Mn$_{0.95}$B$_{0.05}$O$_{3-\delta}$, were chosen for study along with their respective parent compounds.

**Chemical compatibility**

For CaMn$_{1-x}$M$_x$O$_{3-\delta}$, the XRD patterns of the samples and CGO10 mixtures show no evidence of additional diffraction peaks due to impurities at temperatures up to 900 ºC (Figure 6). At 1000 ºC, however, there were weak extra peaks, indicating some reaction between the system and CGO. The reaction product has been identified as Ca$_4$Mn$_3$O$_{10}$ (PDF 089-0815). The level of reaction products increased with the firing temperature, up to 1100 ºC, although its fraction is relatively small compared to the majority phases. For
La$_{1-x}$Sr$_x$Mn$_{1-x}$B$_x$O$_{3-\delta}$ there was no evidence of secondary phases at any temperature examined (Figure 7).

**Area-specific resistance study**

*CaMn$_{1-x}$M$_x$O$_{3-\delta}$*

For the cathode testing, two fixing temperatures were studied: 900 and 1000°C. Initially attempts were made to deposit the cathode material on its own onto the CGO electrolyte surface, but these experiments resulted in a poor adhesion and high ASR values at all temperatures studied. Subsequently, composite cathodes were examined. Using a mixture of calcium manganite and electrolyte (1:1 wt%) the cathode showed good adherence to the electrolyte surface.

In Figure 8, we show the impedance spectra for the symmetrical cells with CaMnO$_3$/CGO10 and CaMn$_{0.95}$P$_{0.05}$O$_{3.8}$/CGO10 cathodes. The spectra can be decomposed into two overlapped contributions, a high frequency arc (assigned to the transport of O$^{2-}$ ions and intermediate species through the cathode and at the cathode/electrolyte interface), and a low frequency arc (assigned to the competitive reactions at the TPB: adsorption, transfer of species and surface diffusion) [29]. As can be seen, the two phenomena are much smaller for the P-doped sample, which can be explained by the increase in electronic conductivity and likely also oxide ion conductivity (due to the generation of oxide ion vacancies caused by the oxyanion doping).

The ASR values were observed to be high at the higher fixing temperature (1000 ºC): 1.50 Ω·cm$^2$ at 800°C. This behaviour is likely due to the presence of secondary phases because of the reactivity at 1000°C between calcium manganites and CGO10, already
outlined in the chemical compatibility section. At the lower fixing temperature (900°C) the ASR values were far smaller. The dependence of the area-specific resistance (ASR) with temperature for these samples is shown in Figure 9. At 800°C, the values obtained for x=0.05, for B and P-doping, were 0.37 and 0.30 Ω·cm² respectively. These results entail a significant improvement with respect to the undoped compound (CaMnO₃), 1.50 Ω·cm² at 800°C. These results therefore show the beneficial effects of oxyanion doping on both the conductivity of CaMnO₃ as well as its performance as a SOFC cathode.

\[ \text{La}_{1-y}\text{Sr}_y\text{Mn}_{1-x}\text{B}_x\text{O}_{3-\delta} \]

For the cathode testing, two fixing temperatures were studied: 1000 and 1100°C. Initially attempts were made to deposit the cathode material on its own onto the CGO electrolyte surface, but as for the CaMnO₃ systems, these experiments resulted in a poor adhesion and high ASR values at all temperatures. Therefore a mixture of \( \text{La}_{1-y}\text{Sr}_y\text{Mn}_{1-x}\text{B}_x\text{O}_{3-\delta} \) and electrolyte (1:1 wt%) was examined. At a fixing temperature of 1000°C, poor adhesion was again observed along with high ASR values. These problems were overcome by moving to a higher fixing temperature (1100°C), and the dependences of the area-specific resistance (ASR) with temperature for these electrodes are shown in Figure 10. At 800°C, the values obtained for \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.95}\text{B}_{0.05}\text{O}_{3-\delta} \) and \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.95}\text{B}_{0.05}\text{O}_{3-\delta} \), were 0.33 and 0.39 Ω·cm², respectively. These results entail an improvement with respect to the undoped compounds, \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3-\delta} \) and \( \text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_{3-\delta} \), which gave ASR values of 0.64 and 0.56 Ω·cm² respectively. Therefore, despite the lower electronic conductivity, an improvement in the ASR values was observed, which may be due to an increase in ionic conductivity due to the creation of oxide ion vacancies on borate doping.

4. Conclusions
CaMn$_{1-x}$M$_{x}$O$_{3-\delta}$ (M = B and P) and La$_{1-y}$Sr$_y$Mn$_{1-x}$B$_x$O$_{3-\delta}$ cathode materials have been prepared by solid state reaction. For the former, a large improvement in the conductivity was observed on borate, phosphate doping. The best conductivity values were achieved for CaMn$_{0.95}$P$_{0.05}$O$_{3-\delta}$, 43.0·S·cm$^{-1}$ at 800ºC. ASR values were determined for composites of these cathode materials in combination with 50 wt% CGO10 on dense CGO10 pellets. The values obtained at 800ºC, were 1.50, 0.37 and 0.30 $\Omega$·cm$^2$ for CaMnO$_3$, CaMn$_{0.95}$B$_{0.05}$O$_{3-\delta}$ and CaMn$_{0.95}$P$_{0.05}$O$_{3-\delta}$, respectively, demonstrating the improved performance on borate/phosphate doping. For the La$_{1-y}$Sr$_y$Mn$_{1-x}$B$_x$O$_{3-\delta}$ system, the electronic conductivity decreased on doping with borate, although the ASR values on dense CGO10 pellets showed an improvement, which may be due to enhanced oxide ion conductivity. Thus, these data show the first results for improvement in SOFC cathode performance through oxyanion doping, and suggest that further studies on other perovskite cathode materials are warranted.

Acknowledgements

We would like to express thanks to EPSRC for funding (grant EP/I003932). The Bruker D8 diffractometer and Netzsch STA 449 F1 Jupiter Thermal Analyser and solid state MAS NMR instrumentation used in this research were obtained through the Science City Advanced Materials project: Creating and Characterising Next generation Advanced Materials project, with support from Advantage West Midlands (AWM) and part funded by the European Regional Development Fund (ERDF).

References
1. A. Orera, P.R. Slater; *Chem. Mater.* 2010, **22**, 675.


Table 1. Cell parameters for CaMn$_{1-x}$M$_x$O$_{3-\delta}$ (M=B and P).

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Table 2. Cell parameters for La$_{1-y}$Sr$_y$Mn$_{1-x}$B$_x$O$_{3-δ}$ [y=0.3, 0.4 (hexagonal cell) and 0.5 (tetragonal cell), x=0, 0.05 and 0.10]
Table 3. Oxygen deficiencies (δ) and Mn oxidation states (from TGA) and conductivity data at 700°C for CaMn$_{1-x}$M$_x$O$_{3-\delta}$ (M=B and P; x=0, 0.025 and 0.05) and La$_{1-y}$Sr$_y$Mn$_{1-x}$B$_x$O$_{3-\delta}$ (x=0 and 0.05)

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<td>0 0.025 0.05</td>
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<tr>
<td>Oxygen deficiency (δ)</td>
<td>0.04 0.07 0.07</td>
<td>0.08 0.15</td>
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<tr>
<td>Oxidation state</td>
<td>3.93 3.88 3.90</td>
<td>3.82 3.62</td>
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<tr>
<td>Conductivity at 700°C (S cm$^{-1}$)</td>
<td>3.24 20.70 19.54</td>
<td>36.92 48.44</td>
</tr>
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Table 4. $^{11}$B MAS NMR spectral parameters used for the simulated/deconvoluted data for CaMn$_{0.95}$B$_{0.05}$O$_{3-\delta}$.

<table>
<thead>
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<th>Shift δ (ppm ±5)</th>
<th>Gaussian Broadening (kHz ±1)</th>
<th>Integrated Intensity (%) ±2</th>
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<tr>
<td>481</td>
<td>15</td>
<td>37</td>
</tr>
<tr>
<td>152</td>
<td>11</td>
<td>39</td>
</tr>
<tr>
<td>-214</td>
<td>20</td>
<td>24</td>
</tr>
</tbody>
</table>
Figure captions

**Figure 1.** X-ray diffraction patterns for a) CaMn$_{0.95}$O$_{3-\delta}$; b) CaMnO$_{3-\delta}$; c) CaMn$_{0.95}$B$_{0.05}$O$_{3-\delta}$; and d) CaMn$_{0.90}$B$_{0.10}$O$_{3-\delta}$. Impurities highlighted with arrows.

**Figure 2.** Solid state $^{11}$B MAS NMR spectra for CaMn$_{0.95}$B$_{0.05}$O$_{3-\delta}$ collected at low field (2.35 T) and at ambient temperature.

**Figure 3.** X-ray diffraction patterns for a) La$_{0.6}$Sr$_{0.4}$Mn$_{0.95}$O$_{3-\delta}$; b) La$_{0.6}$Sr$_{0.4}$MnO$_{3-\delta}$; c) La$_{0.6}$Sr$_{0.4}$Mn$_{0.95}$B$_{0.05}$O$_{3-\delta}$; and d) La$_{0.6}$Sr$_{0.4}$Mn$_{0.90}$B$_{0.10}$O$_{3-\delta}$. Impurities highlighted with arrows.

**Figure 4.** Conductivity plot for CaMnO$_3$ (★), CaMn$_{0.975}$B$_{0.025}$O$_{3-\delta}$ (□), CaMn$_{0.95}$B$_{0.05}$O$_{3-\delta}$ (■), CaMn$_{0.975}$P$_{0.025}$O$_{3-\delta}$ (○) and CaMn$_{0.95}$P$_{0.05}$O$_{3-\delta}$ (●).

**Figure 5.** Arrhenius plots of log$\sigma_T$ for La$_{0.7}$Sr$_{0.3}$MnO$_{3-\delta}$ (□), La$_{0.6}$Sr$_{0.4}$MnO$_{3-\delta}$ (○), La$_{0.5}$Sr$_{0.5}$MnO$_{3-\delta}$ (△), La$_{0.7}$Sr$_{0.3}$Mn$_{0.95}$B$_{0.05}$O$_{3-\delta}$ (■), La$_{0.6}$Sr$_{0.4}$Mn$_{0.95}$B$_{0.05}$O$_{3-\delta}$ (●) and La$_{0.5}$Sr$_{0.5}$Mn$_{0.95}$B$_{0.05}$O$_{3-\delta}$ (▲).

**Figure 6.** XRPD patterns for CaMn$_{0.95}$B$_{0.05}$O$_{3-\delta}$, Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (CGO10) and CaMn$_{0.95}$B$_{0.05}$O$_{3-\delta}$/Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ powder mixtures (1:1 wt.%) at room temperature (RT) and after firing between RT and 1100 ºC. Ca$_4$Mn$_5$O$_{10}$ is highlighted with an arrow.

**Figure 7.** XRPD patterns for La$_{0.6}$Sr$_{0.4}$Mn$_{0.95}$B$_{0.05}$O$_{3-\delta}$, Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (CGO10) and La$_{0.6}$Sr$_{0.4}$Mn$_{0.95}$B$_{0.05}$O$_{3-\delta}$/Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ powder mixtures (1:1 wt.%) at room temperature (RT) and after firing between RT and 1100 ºC.

**Figure 8.** Impedance spectra of the symmetrical cells for CaMnO$_3$ (□) and CaMn$_{0.95}$P$_{0.05}$O$_{3-\delta}$ (■)/CGO10 composites at 750ºC. The serial resistance was subtracted for better comparison of the spectra.
**Figure 9.** Temperature dependence of the area-specific resistance (ASR) values for CaMnO$_3$-CGO10 (□), CaMn$_{0.95}$B$_{0.05}$O$_{3-\delta}$-CGO10 (○) and CaMn$_{0.95}$P$_{0.05}$O$_{3-\delta}$-CGO10 (△) deposited at 900°C over the CGO10 electrolyte at open circuit voltage.

**Figure 10.** Temperature dependence of the area-specific resistance (ASR) values for La$_{0.7}$Sr$_{0.3}$MnO$_{3-\delta}$-CGO10 (■), La$_{0.6}$Sr$_{0.4}$MnO$_{3-\delta}$-CGO10 (●), La$_{0.5}$Sr$_{0.5}$MnO$_{3-\delta}$ (△), La$_{0.7}$Sr$_{0.3}$Mn$_{0.95}$B$_{0.05}$O$_{3-\delta}$-CGO10 (□) and La$_{0.6}$Sr$_{0.4}$Mn$_{0.95}$B$_{0.05}$O$_{3-\delta}$-CGO10(○) deposited at 1100°C over the CGO10 electrolyte at open circuit voltage.
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Figure 4. Conductivity plot for CaMnO₃ (★), CaMn₀.₉₇₅B₀.₀₂₅O₃₋δ (□), CaMn₀.₉₅B₀.₀₅O₃₋δ (■), CaMn₀.₉₇₅P₀.₀₂₅O₃₋δ (○) and CaMn₀.₉₅P₀.₀₅O₃₋δ (●).
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