OXYGEN STOICHIOMETRY IN CATION DEFICIENT (La, Sr)$_{1-x}$MnO$_3$ SOFC CATHODE MATERIALS

B. Zachau-Christiansen, T. Jacobsen & S. Skaarup
Department of Chemistry
Technical University of Denmark
DK-2800 Lyngby, Denmark.

ABSTRACT

The variation of oxygen stoichiometry with oxygen partial pressure is determined for perovskites, ABO$_3$, with the general composition: (La$_{1-x}$Sr$_x$)$_{1-z}$MnO$_{3+y}$, $x<0.15$, $0<z<0.10$, and $y=0$. The measurements are performed as linear sweep voltammetry on an oxygen pumping cell, where the oxygen partial pressure is controlled by the imposed potential. It is found that the oxygen stoichiometry and hence the defect chemistry is different whether A-site charge deficiency is established by Sr-doping or by A-site vacancies. Furthermore, A-site deficient lanthanum strontium manganates expel a secondary phase of manganese oxide when exposed to low oxygen partial pressures. The presence of small amounts of secondary phase is observed and identified by its reoxidation peak. The amount of this foreign phase is determined by the charge used for its oxidation.

INTRODUCTION

Lanthanum manganates and strontium doped lanthanum manganates occur as distorted perovskites (ABO$_3$) and represent the classical choice of electrode material for the positive electrode in high temperature solid oxide fuel cells (SOFC). The electronic and ionic transport properties of these materials and hence the extension of the effective three-phase contact region in electrodes is determined by the defect chemistry. The doped lanthanum manganates constitute a group of materials which combines a high electrocatalytic activity for oxygen reduction and a high electronic conductivity. Furthermore the lanthanum manganates belong to a rare class of the perovskites exhibiting oxidative nonstoichiometry in air; besides LaMnO$_{3+y}$ this class counts members such as Ba$_{0.8}$La$_{0.2}$TiO$_{3+y}$, LaVO$_{3+y}$ and at high temperatures EuTiO$_{3+y}$ (1). The oxygen stoichiometry is considered to influence the electrocatalytic properties with respect to oxygen reduction appreciably, as oxygen vacancies in the perovskite will enhance the transport of oxygen ions either on the surface or through the bulk of the electrode material. However, in air the concentration of oxygen vacancies is limited due
to the excess oxygen nonstoichiometry, and the detailed mechanism of the oxygen reaction is not fully understood (2,3).

It is generally found that lanthanum manganates with or without Sr are stoichiometric in commercial nitrogen gas having an oxygen partial pressure of approximately $10^{-6}$ atm (4-7). Substoichiometric phases $\text{LaMnO}_{3-y}$ containing $\text{Mn}^{2+}$ are formed at reducing oxygen partial pressures until phase separation into multiple phases occurs. The major defects in this range are proposed to be clusters of oxygen vacancies and $\text{Mn}^{2+}$, described as $<\text{Mn}'_{\text{Mn}}-\text{V}^\cdot_{\text{O}}-\text{Mn}''_{\text{Mn}}>$ entities (8,9). This model is supported by the very good agreement between measured and calculated electronic conductivities (10). The information obtained from the variation of the electronic conductivity with oxygen partial pressure in the excess oxygen region is limited. The conductivity is very high and in the range of oxygen partial pressures $10^{-10}$ atm<$p(\text{O}_2)$<1 atm it is practically independent of $p(\text{O}_2)$, indicating that the carrier concentration is constant throughout the oxygen excess region (10,11).

The aim of the present contribution is to investigate the nonstoichiometry and phase composition of lanthanum manganates/manganites in order to obtain a better interpretation of the defect chemistry of these compounds. In practical SOFC electrodes a surplus of manganese is often used to prevent reaction between La from the cathode and $\text{ZrO}_2$ from the electrolyte (12), hence an understanding of the nonstoichiometry of A-site deficient lanthanum manganates is anticipated. The oxygen content is determined at high temperature by slow, linear sweep voltammetry as this method offers a very low detection limit for secondary phases and impurities (13).

EXPERIMENTAL

The oxygen content of a nonstoichiometric oxide can be modified by equilibrating the sample in atmospheres of different oxygen partial pressure:

$$\text{MO}_\xi + \delta/2 \text{O}_2 \rightarrow \text{MO}_{\xi+\delta}$$

In equation [1] $\xi$ denotes the total oxygen content, while $\delta$ is an infinitesimal change of this quantity. In an oxygen pumping cell the partial pressure of oxygen can be varied electrochemically by imposing different potentials across the cell:

$$\text{Pt}, \text{O}_2 | \text{YSZ} | \text{Pt}, \text{MO}_\xi$$

In this cell a sample of $\text{MO}_\xi$ enclosed in a sealed YSZ compartment is used, see fig.1. The oxide sample is contained in a YSZ compartment closed by an alumina disc. Counter (CE), reference (RE) and working (WE) electrodes are platinum painted on the YSZ. The cell is sealed with gold gaskets and pyrex glass (14). Adhesion of Pt electrodes to the YSZ was obtained by annealing in $\text{H}_2/\text{Ar}$ (7:93) before painting with Pt (15). The Pt paint was burnt in the same gas. The cell has a rather small ohmic resistance of 5-10 $\Omega$ at 1000°C. The oxygen partial pressure is determined by the
voltage applied to the cell. The current used to change the stoichiometry is found from the total current by subtraction of the contributions from leaks and from the gas-phase capacity of the cell. The cell is subjected to slow potential scans, 5 μV/s, followed by equilibration periods of $10^4$-$10^5$ s. The differential capacity of a sample is then obtained by averaging the cathodic and the anodic branches of a complete potential cycle before the gas phase contribution is subtracted (16). Experiments are performed at 1000°C.

The samples investigated here are $(La_{1-x}Sr_x)_1-z$MnO$_{3+y}$ (x=0, 0.05, 0.15; -0.02≤z≤0.04) prepared from acetates at Department of Chemistry, Odense University (5). All samples were cooled very slowly from the reaction temperature of 1100°C, and analyzed for total manganese and oxidation equivalents by KMnO$_4$ titration and iodometry (6). The chemical composition of the lanthanum perovskites will throughout this work be given with the stoichiometric coefficient of manganese normalized to 1.00, for consistency or clarity. The smallest structural entity should, however, be based on a normalization of the oxygen coefficient to 3.00 in the oxygen excess region, and based on either the A-ion or the B-ion occupancy in the region of oxygen deficit (1).

RESULTS AND DISCUSSION

The most widely used cathode material for the air electrode in a SOFC is lanthanum manganate with 15% Sr doping on the A-site. A surplus of manganese is used in the fabrication of SOFC electrodes to prevent reaction between La from the cathode and ZrO$_2$ from the electrolyte (12). Two samples with 15% Sr doping on the A-site but with different A/B ratios are investigated: $La_{0.83}Sr_{0.15}MnO_{3+0.02}$ (NS) and $La_{0.87}Sr_{0.15}MnO_{3.10}$ (S) as analyzed at room temperature (6). The NS sample was prepared with a nominal 5% excess of Mn. X-ray diffraction showed it to contain 1.9% (w/w) Mn$_3$O$_4$ and the composition given is corrected for the content of this secondary phase (5). Fig.2 shows the results of linear sweep voltammetry on these samples. For NS two cycles are shown: The first cycle is performed in the potential interval [-0.35;0.035] V vs air, while the potential region spanned is increased to [-0.50;0.035] V vs air in the second. The symmetry between the anodic and the cathodic branches of the first cycle is renowned and shows that the oxygen is exchanged from a homogeneous phase with variable oxygen stoichiometry. As the secondary phase of Mn$_3$O$_4$ is reduced to MnO at -0.375 V vs air (17) this component is only visible in the second cycle. The lack of overlap between the anodic and the cathodic branches of the sweeps indicates a reaction involving two co-existing phases (i.e. Mn$_3$O$_4$+MnO), as oxidation is only initiated when the potential has passed -0.375 V vs air in ascending direction. Integration of the current in the anodic peak of the second cycle leads to a Mn$_3$O$_4$ content of 2.2% (w/w), which is very close to the amount found at room temperature (1.9% (w/w)). This shows that the phase limit of the perovskite in this range of oxygen partial pressures is practically independent of temperature (25-1000°C). The compound S ($La_{0.87}Sr_{0.15}MnO_{3+y}$) is seen not to contain Mn$_3$O$_4$, but it has an extra set
of reversible peaks, indicating ordering phenomena. Comparing the actual variation in oxygen content at 1000°C, fig.3, it is seen that stoichiometric coefficients of oxygen in air at 1000°C are 3.03 and 3.02 for La$_{0.83}$Sr$_{0.17}$MnO$_{3+y}$ (NS) and La$_{0.87}$Sr$_{0.13}$MnO$_{3+y}$ (S), respectively. Both curves are normalized to y=0 at -0.35 V vs air as the slopes of the sweeps exhibit local minima inferring that completed lattices exist at this potential, corresponding to an oxygen partial pressure $p(O_2)=6\cdot10^{-7}$ atm. As the chemical compositions in the oxygen excess region can be formulated as (La$_{0.85}$Sr$_{0.15}$)$_{0.98}$MnO$_{3+y}$ (NS) and (La$_{0.85}$Sr$_{0.15}$)$_{1.02}$MnO$_{3+y}$ (S) these results indicate that the La content or the A-site occupancy has limited influence on the oxygen excess at high temperature. The difference in formal charge on the A-site between the samples NS and S is 0.11, a difference which would be expected to be accompanied by a difference of $\Delta y=0.055$ for the oxygen stoichiometry in ABO$_{3+y}$. This conclusion is valid for samples with a Sr doping smaller than 0.30 Sr/formula unit (6).

The influence of the A-site occupancy was further studied in lanthanum manganates without Sr doping. The samples LM98 and LM96 were prepared with a nominal manganese excess of 5% and 10%, respectively. At room temperature the chemical compositions were found to be La$_{0.98}$MnO$_{3.07}$ (LM98) and La$_{0.96}$MnO$_{3.03}$ + 1% (w/w) Mn$_3$O$_4$ (LM96) (5). Linear potential sweeps on these two samples are shown in fig.4 and fig.5. Each sweep is initiated at gradually lower potentials. The samples are equilibrated 10$^5$ s at the lower potential limit before each scan and 5$\cdot10^4$ s at the high potential before reversal of the scan direction. In the potential range [-0.5,0.035] V vs air, fig.4, LM98 is seen to contain only the perovskite phase with a homogeneous, reversible oxygen excess region. When the sample is exposed to more reducing conditions increasing amounts of MnO are expelled. The MnO is identified by the potential, -0.375 V vs air (17), where the reoxidation to Mn$_2$O$_4$ is initiated. As the sweeps contain no cathodic counterpart of this reaction, it is concluded that the Mn$_3$O$_4$ is redissolved into the perovskite phase at high oxygen partial pressure. The behaviour of LM96 (La$_{0.96}$MnO$_{3.03}$, fig.5) is somewhat different as this sample initially contains 1.2% (w/w) which is never reabsorbed into the perovskite lattice in air. When LM96 is reduced below -0.5 V vs air it segregates more MnO, similar to the behaviour of LM98. The actual amount of "permanent" Mn$_2$O$_4$ is very close to the amount of Mn$_3$O$_4$ found at room temperature, 1% (w/w). This finding establishes the stability limit of the perovskite to A/B=0.96 in air in the temperature range 25-1000°C.

In Table I the composition of the samples after equilibration at the low oxygen partial pressures is shown. The composition of the perovskites at the low potentials is calculated from the charge used for reduction of the homogeneous phase in the cathodic sweep, i.e. excluding the contribution from the MnO formation. This correction is determined from the subsequent oxidation to Mn$_2$O$_4$. It is seen that for both samples increasing amounts of MnO are formed along with a transformation of the perovskite from a substoichiometric - with respect to the A/B ratio - composition to a lanthanum rich phase. It is seen that the extra amounts of MnO formed at -0.75 and -1.00 V vs air are equal, and within the limit of accuracy the compositions of the perovskites are...
similar, depending only on the oxygen partial pressure. This finding is in accordance with the phase rule stating that the composition and hence the A/B-ratio in the 3-phase 3-component system of La, Mn, and O₂ is determined by only two extra parameters: oxygen pressure and temperature.

Table I. Phase composition of reduced lanthanum manganates.

| Sample | Potential [V vs air] | Oxygen pressure [atm] | Mole fraction of MnO | Mole fraction of LaₓMnO₃⁺y | Composition of LaₓMnO₃⁺y |
|--------|----------------------|----------------------|---------------------|--------------------------|--------------------------|
| LM96   | -0.50                | 2.5·10⁻⁹             | 0.04                | 0.96                     | La₀.⁹₆MnO₃₀.⁰₀         |
| LM96   | -0.75                | 2.7·10⁻¹³            | 0.07                | 0.93                     | La₀.⁹⁹MnO₂₉.⁹⁹         |
| LM96   | -1.00                | 3.0·10⁻¹⁷            | 0.09                | 0.91                     | La₁.₀¹MnO₂₉.₃₉         |
| LM98   | -0.50                | 2.5·10⁻⁹             | 0.00                | 1.00                     | La₀.⁹₈MnO₃₀.⁰₀         |
| LM98   | -0.75                | 2.7·10⁻¹³            | 0.03                | 0.97                     | La₁.₀¹MnO₂₉.₉₉         |
| LM98   | -1.00                | 3.0·10⁻¹⁷            | 0.05                | 0.95                     | La₁.₀₃MnO₂₉.₄₄         |

For both LM96 and LM98 it is seen that there is no extra amount of Mn₃O₄ available for reduction as the potential passes -0.375 V vs air in cathodic direction. This means that all the MnO expelled during exposure to low oxygen partial pressure is redissolved into the perovskite when equilibrated air.

The implication of this is an apparent asymmetry in the oxidation/reduction behaviour when traversing both the super- and the substoichiometric domains. Formally the reaction sequence can be described by the following scheme:

Reduction:

\[
\begin{align*}
\text{La}_x\text{MnO}_{3+y} & \rightarrow \text{La}_x\text{MnO}_3 + \frac{y}{2} \text{O}_2 \\
\text{La}_x\text{MnO}_3 & \rightarrow (1-v) \text{La}_{\frac{x}{(1-v)}}\text{MnO}_{3-u} + v \text{MnO} + \frac{(2v+u(1-v))}{2} \text{O}_2 
\end{align*}
\]

Oxidation:

\[
\begin{align*}
(1-v) \text{La}_{\frac{x}{(1-v)}}\text{MnO}_{3-u} + u(1-v)/2 \text{O}_2 & \rightarrow (1-v) \text{La}_{\frac{x}{(1-v)}}\text{MnO}_3 + v \text{MnO} + v/6 \text{O}_2 \\
(1-v) \text{La}_{\frac{x}{(1-v)}}\text{MnO}_3 + v/3 \text{Mn}_3\text{O}_4 + (2v/3+y)/2 \text{O}_2 & \rightarrow \text{La}_x\text{MnO}_{3+y}
\end{align*}
\]

During reduction the stoichiometric composition is obtained before the formation of the substoichiometric compositions accompanied by segregation of MnO is initiated. The MnO is continuously expelled as no separate reduction peak in the linear potential sweeps is observed. When the sample is oxidized a stoichiometric composition with a different A/B ratio is initially reached, and then the MnO is oxidized to Mn₃O₄. After
this the Mn$_3$O$_4$ is reabsorbed into the perovskite along with the formation of excess oxygen compositions.

When cycled within the oxidative nonstoichiometry region the amount of Mn$_3$O$_4$ is unchanged and the behaviour of the perovskites can be examined. Fig.6 depicts the actual oxygen excess for the pure lanthanum manganates studied here. For comparison the variation of the oxygen stoichiometry for samples of Sr-doped lanthanum manganates, La$_{0.98}$MnO$_{3.11}$, (La$_{0.95}$Sr$_{0.05}$)$_{0.97}$MnO$_{3.05}$ and (La$_{0.85}$Sr$_{0.15}$)$_{1.02}$MnO$_{3.10}$ also determined, is included. According to the sweeps all samples, (La,Sr)$_2$MnO$_{3+y}$, are normalized to y=0 at a potential of -0.35 V vs air i.e. p(O$_2$)=6·10$^{-7}$ atm.

For the pure lanthanum manganates the variation of the oxygen stoichiometry is seen to be similar and almost independent of the A-site occupancy. For the samples investigated here the total charge on the A-site varies from 2.88 over 2.94 to 3.06 for a B-site stoichiometric coefficient normalized to 1. Doping with Sr is another way of reducing the total A-site charge: One A-site vacancy, V$_{La}$, will be equivalent to exchange with 3 Sr-atoms, Sr$_{La}$. For the Sr doped samples in fig.6 the total A-site charges are 2.94 (LSM00), 2.86 (LSM05) and 2.91 (LSM15). It is seen that doping with Sr has a much more pronounced effect on the oxygen stoichiometry than simple A-site vacancies, despite the similar total charges on the A-site. Apparently, doping with Sr leads to a stabilization of the lattice, hence reducing the ability to accept oxygen in excess. By considering the similar ionic radii of Sr[XII]$^{2+}$ and La[XII]$^{3+}$ of 1.44 Å and 1.36 Å, respectively (18), it is natural that a Sr$_{La}$ ion will match a La$_{La}^x$ site much better than the vacancy V$_{La}$.

CONCLUSION

In air in the temperature range 25-1000°C lanthanum manganates will expel Mn$_3$O$_4$ when the A/B is less than 0.96. In the oxygen deficient region the critical A/B ratio increases with decreasing oxygen pressure and consequently a secondary MnO phase may be segregated. In the oxygen excess region introduction of A-site vacancies has little effect on the oxygen stoichiometry, whereas reduction of the A-site charge, accomplished by doping with ions of lower valency, is compensated by a reduction of the superstoichiometry. The phase segregation might influence the long term stability of a working SOFC if large overvoltage variations are encountered.

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Fig. 1 Electrochemical cell.

Fig. 2 Voltammograms for La$_{0.83}$Sr$_{0.15}$MnO$_{3+y}$ (NS) + Mn$_3$O$_4$ (1% w/w) and La$_{0.87}$Sr$_{0.15}$MnO$_{3+y}$ (S). Sweep rate: 5 µV/s, Temperature: 1000°C. Potential ranges indicated. Gas phase capacity subtracted.

Fig. 3 Oxygen stoichiometry for La$_{0.83}$Sr$_{0.15}$MnO$_{3+y}$ (NS) and La$_{0.87}$Sr$_{0.15}$MnO$_{3+y}$ (S). Temp.: 1000°C.
Fig. 4 Voltammograms for La$_{0.98}$MnO$_{3.07}$ (LM98). Sweep rate: 5 $\mu$V/s, Temperature: 1000°C. Potential ranges indicated. Gas phase capacity subtracted.

Fig. 5 Voltammograms for La$_{0.96}$MnO$_{3.03}$ (LM96) + Mn$_3$O$_4$ (1% w/w). Sweep rate: 5 $\mu$V/s, Temperature: 1000°C. Potential ranges indicated. Gas phase capacity subtracted.
Fig. 6 Oxygen stoichiometry for \((\text{La}_{1-x}\text{Sr}_x)_{1-z}\text{MnO}_3+y\). Temperature: 1000°C. \(x\) and \(z\) indicated.