Synthesis and electrical characterisation of doped perovskite titanates as potential anode materials for solid oxide fuel cells

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This work reports the synthesis and electrical characterisation over a range of oxygen partial pressures (10^{-20}–1 atm) of the A-site deficient perovskites $Sr_{1-3x/2}La_xTiO_{3-\delta}$, with a view to establishing their potential as anode materials for solid oxide fuel cells. Single phase samples were observed for synthesis in air for $0 \leqslant x \leqslant 0.6$, and the materials remained phase pure for both high and low oxygen partial pressures at the measurement temperature of 930 °C. Good electrical conductivity, which increased with increasing La content, was observed on reduction in low oxygen partial pressures, with values as high as 7 S cm^{-1} [$P(O_2) = 10^{-20}$ atm], similar to values observed for the related system, $Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}$, examined previously. The conductivity of the fully reduced samples showed metallic character from 100 to 930 °C. As the oxygen partial pressure was raised, the conductivity dropped, showing an approximate $[P(O_2)]^{-1/6}$ dependence for porous samples. New samples, $Sr_{1-y/2-3x/2}La_xTi_{1-y}Nb_yO_{3-\delta}$, with both La and Nb substitutions, were also studied, and these phases showed similar electrical behaviour. Further results for the $Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}$ system are presented and compared with the La doped systems.

Solid oxide fuel cells are currently at the forefront of research into new generations of energy conversion systems, owing to their high efficiency and environmentally friendly nature. Considerable attention has been focused on these systems, particularly on the electrode front, where new materials with improved properties are being sought. Our objective has been to develop new anode materials to eliminate the problems associated with the current anode, Ni/YSZ cermet, notably sintering of Ni at fuel cell temperatures, and problems with using natural gas as a fuel due to carbon build up and sulfur poisoning. In this respect, oxides have been targeted, since these have several advantages over metals, in that they are potentially less likely to promote coking and less likely to suffer from sulfur poisoning.

In previous work we have studied the synthesis and electrical characterisation of titanate spinels.[1] We are currently studying perovskite materials as potential anodes. Perovskites have general formula ABO_3 (A = large 12-coordinate cation, B = small 6-coordinate cation). Perovskites are good candidate anodes because materials with this structure type are known to exhibit suitable characteristics for efficient anode operation such as high electronic conductivity, high oxide ion conductivity and good catalytic activity. We have focused on studying doped $SrTiO_3$, substituting at both the A and B sites. Our aim was to synthesise materials which were stable in both oxidizing and reducing conditions, showing good conductivity in low oxygen partial pressures.

In earlier work we reported results for perovskite niobate-titanates.[2] New phases of composition $Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}$ were prepared, which showed good electrical conductivity in low oxygen partial pressures, up to 5.6 S cm^{-1} [$P(O_2) = 10^{-18}$ atm at 930 °C] for $x = 0.25$. In this system the higher charge on the B sites introduced by doping Nb for Ti is balanced by introducing a Sr deficiency on the A site. These samples were synthesised in air and then reduced *in situ* to introduce some Ti^{3+}/Nb^{4+} and consequent electronic conduction, and were structurally stable in both reducing and oxidising atmospheres.

A related system that we are working on is the perovskite strontium–lanthanum titanates. In this case La doping on the A site is introduced, and charge balance is once more attained by an A site deficiency, giving a composition $Sr_{1-3x/2}La_xTiO_3$. These samples are then reduced *in situ* similarly to the $Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}$ samples to give an oxygen deficient perovskite, $Sr_{1-3x/2}La_xTiO_{3-\delta}$ containing some Ti^{3+} and thus introducing electronic conduction.

In this paper we report the synthesis and electrical characterisation of the $Sr_{1-3x/2}La_xTiO_{3-\delta}$ samples. In addition the synthesis in air and electrical characterisation is reported for the new series of niobate–titanates, $Sr_{1-y/2-3x/2}La_xTi_{1-y}Nb_yO_{3-\delta}$. The results are compared with those for the $Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}$ system examined previously,[2] and further results on this system are also presented.

Experimental

Synthesis of $Sr_{1-3x/2}La_xTiO_{3-\delta}$

High-purity $SrCO_3$, La_2O_3, and TiO_2 were intimately mixed in the appropriate ratios, and heated at 925 °C for 15 h in air, reground, and reheated at 1440 °C for 24 h. Single phase samples were observed by powder X-ray diffraction (Stoe Stadi diffractometer) for $0 \leqslant x \leqslant 0.6$, in agreement with a study by Tien and Hummel.[3] In order to achieve higher La levels, *i.e.* to obtain the Sr free end-member $La_{0.67}TiO_3$, synthesis under reducing conditions is required.[4] The $Sr_{1-y/2-3x/2}La_xTi_{1-y}Nb_yO_{3-\delta}$ samples were made using identical conditions to $Sr_{1-3x/2}La_xTiO_{3-\delta}$, employing high-purity Nb_2O_5. The synthesis of samples with $y = 0.2$, 0.25, and 0.4 were attempted. For low La levels, $x \leqslant 0.2$, nearly single phase samples were observed, with TiO_2 appearing as a small impurity. This impurity could be eliminated by adding a small excess of Sr (≈ 0.05 Sr per formula unit). For higher La levels, $x > 0.2$, $LaNbTiO_6$ was observed as an impurity, demonstrating that the solubility limit had been exceeded.

The conductivity measurements were made using the conventional four-probe dc technique. Dense pellets (1.3 cm diameter) of each sample (*ca.* 80–90% theoretical) were obtained by pressing at 5000 kg cm^{-2} and sintering at 1440 °C for 20 h. Pieces of Pt foil attached across the diameter of the pellets by Pt paste were used as contacts, and were wound onto Pt wires. The sample was reduced in situ under H_2–Ar (5% : 95%) for at least 24 h prior to measurement. Oxygen was then allowed to leak into the furnace over a period of 2–3 days and the conductivity followed with changing oxygen partial pressure (measured using a YSZ sensor). Measurements were made at a temperature of 930 °C. After completing the measurements the samples were re-reduced to confirm that a similar electrical conductivity was achieved, and then conductivity measurements were made on this sample in H_2–Ar [$P(O_2)=10^{-20}$ atm] from 930 °C down to room temperature to determine the temperature dependence of the conductivity of the reduced phases.

Thermogravimetry to determine the oxygen contents of the reduced samples was performed using a TA instruments thermal analyser SDT 2960. Reduced samples were oxidised by heating at 10 °C min^{-1} up to 930 °C in O_2, held for 150 min followed by cooling at 5 °C min^{-1} to 550 °C, at which temperature they were held for 30 min before cooling to room temperature at 10 °C min^{-1}.

Results

Cell parameters for the $Sr_{1-3x/2}La_xTiO_{3-\delta}$ samples as prepared, and after reduction in H_2–Ar at a temperature of 930 °C are given in Table 1. As the La content increases, the unit cell contracts, in accord with the smaller size of La compared to Sr (1.32 *vs.* 1.44 Å[5]). The $x=0.6$ sample shows additional peaks to the simple cubic perovskite cell which could be indexed on an expanded unit cell. This is in agreement with previous reports where the expanded cell was attributed to ordering of the cation vacancies as the composition $La_{2/3}TiO_3$ is approached.[4] Cell parameters for the $Sr_{1-y/2-3x/2}La_xTi_{1-y}Nb_yO_{3-\delta}$ samples prepared are also given in Table 1. On reduction all samples exhibited an approximate expansion in unit-cell parameter of 0.10%. This increase in cell was significantly less than in the purely Nb-doped system where expansions of greater than 0.15% were observed.[2]

Chemical compatibility of these titanates with yttria stabilised zirconia (YSZ) was tested by intimately mixing 1 : 1 (by mass) mixtures of YSZ and pre-reacted $Sr_{0.4}La_{0.4}TiO_3$, pressing into pellets and firing at 1000 °C for 24 h in H_2–Ar (5% : 95%). Powder X-ray diffraction indicated no reaction under these conditions, although it is possible that on prolonged heating $La_2Zr_2O_7$ would form, as found for the $La_{1-x}Sr_xMnO_3$ perovskite which is the common cathode material for solid oxide fuel cells.

Four-probe dc conductivity measurements of dense pellets recorded at 930 °C over a wide range of oxygen partial pressures (10^{-20}–1 atm) are shown in Fig. 1 for the $Sr_{1-3x/2}La_xTiO_{3-\delta}$ samples and in Fig. 2 for the $Sr_{1-y/2-3x/2}La_xTi_{1-y}Nb_yO_{3-\delta}$ samples. The corresponding plot for the $Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}$ samples, examined previously, is shown in Fig. 3. The variation of the resistivities of the reduced $Sr_{1-3x/2}La_xTiO_{3-\delta}$ samples with temperature [ambient temperature to 930 °C, $P(O_2)\approx 10^{-20}$ atm] are shown in Fig. 4.

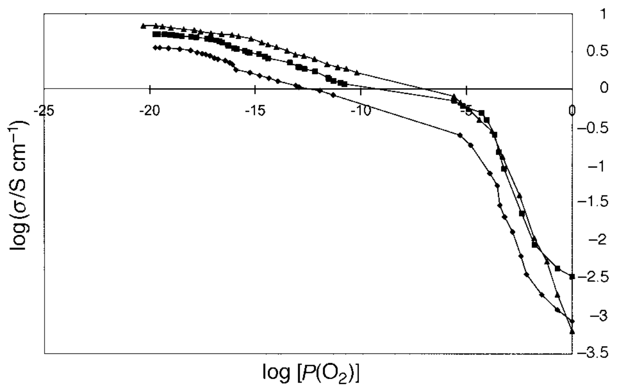

Fig. 1 Plot of log(σ/S cm^{-1}) *versus* log[$P(O_2)$] for dense pellets of $Sr_{1-3x/2}La_xTiO_{3-\delta}$ ($x=0.4$ ◆, 0.5 ■, 0.6 ▲)

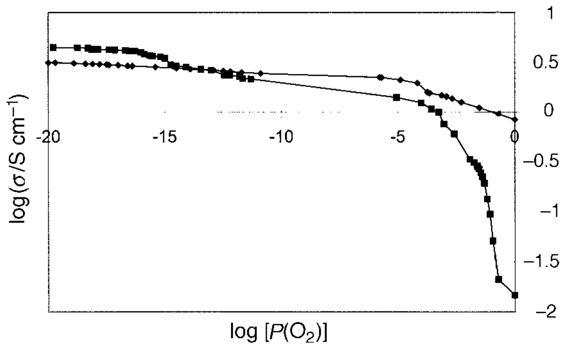

Fig. 2 Plot of log(σ/S cm^{-1}) *versus* log[$P(O_2)$] for dense pellets of $Sr_{0.7-y/2}La_{0.2}Ti_{1-y}Nb_yO_{3-\delta}$ ($y=0.25$ ◆, 0.2 ■)

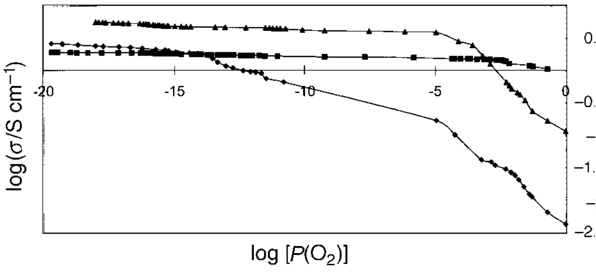

Fig. 3 Plot of log(σ/S cm^{-1}) *versus* log[$P(O_2)$] for dense pellets of $Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}$ ($x=0.15$ ◆, 0.4 ■, 0.25 ▲)

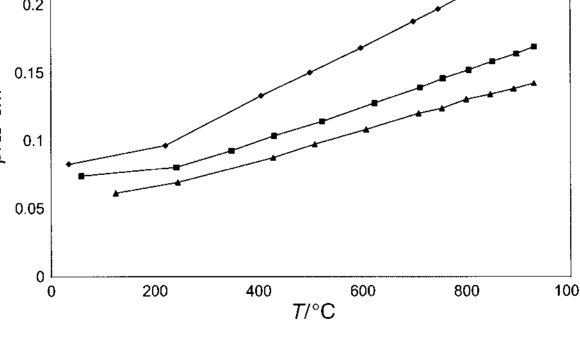

Fig. 4 Plot of resistivity *versus* temperature for the $Sr_{1-3x/2}La_xTiO_{3-\delta}$ samples after reduction at 930 °C ($x=0.4$ ◆, 0.5 ■, 0.6 ▲)

Table 1 Cell parameters for $Sr_{1-3x/2}La_xTiO_{3-\delta}$ and $Sr_{1-y/2-3x/2}La_xTi_{1-y}Nb_yO_{3-\delta}$ samples as-prepared (AP) and after reduction (R) in H_2–Ar (5% : 95%) at 930 °C

sample composition	cell parameter, *a*/Å	*c*/Å
$SrTiO_3$	3.9119(5)	
$Sr_{0.7}La_{0.2}TiO_{3-\delta}$ (AP)	3.9014(3)	
$Sr_{0.4}La_{0.4}TiO_{3-\delta}$ (AP)	3.8940(4)	
$Sr_{0.25}La_{0.5}TiO_{3-\delta}$ (AP)	3.8915(4)	
$Sr_{0.1}La_{0.6}TiO_{3-\delta}$ (AP)	3.883(1)	7.767(8)
$Sr_{0.6}La_{0.2}Ti_{0.8}Nb_{0.2}O_{3-\delta}$ (AP)	3.9108(3)	
$Sr_{0.575}La_{0.2}Ti_{0.75}Nb_{0.25}O_{3-\delta}$ (AP)	3.9147(3)	
$Sr_{0.7}La_{0.2}TiO_{3-\delta}$ (R)	3.9053(1)	
$Sr_{0.4}La_{0.4}TiO_{3-\delta}$ (R)	3.8990(4)	
$Sr_{0.25}La_{0.5}TiO_{3-\delta}$ (R)	3.8951(4)	
$Sr_{0.1}La_{0.6}TiO_{3-\delta}$ (R)	3.887(1)	7.774(7)
$Sr_{0.6}La_{0.2}Ti_{0.8}Nb_{0.2}O_{3-\delta}$ (R)	3.9146(4)	
$Sr_{0.575}La_{0.2}Ti_{0.75}Nb_{0.25}O_{3-\delta}$ (R)	3.9183(4)	

In comparison to the $Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}$ system reported previously, the $Sr_{1-3x/2}La_xTiO_{3-\delta}$ samples show similar good electrical conductivity in low oxygen partial pressures, with the conductivity increasing with increasing La content up to a value of 7 S cm^{-1} [$P(O_2)=10^{-20}$ atm] at 930 °C for $x=0.6$. As in the case of the $Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}$ system the dense pellets of the present samples show a reasonable resistance to re-oxidation particularly at low oxygen partial pressures, although the effect for $Sr_{1-3x/2}La_xTiO_{3-\delta}$ compositions is

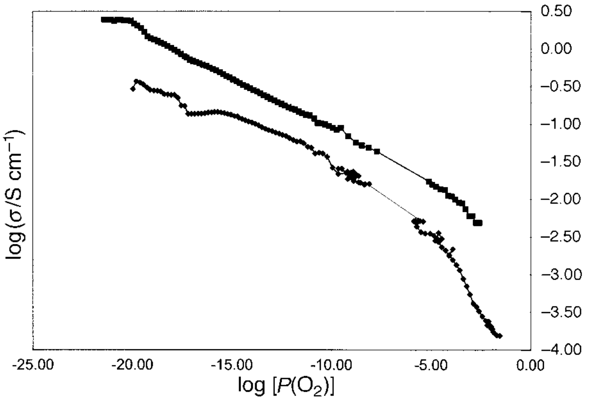

Fig. 5 Plot of $\log(\sigma/\mathrm{S\ cm^{-1}})$ *versus* $\log[P(\mathrm{O_2})]$ for porous pellets of $\mathrm{Sr_{1-3x/2}La_xTiO_{3-\delta}}$ ($x=0.4$ ◆, 0.5 ■)

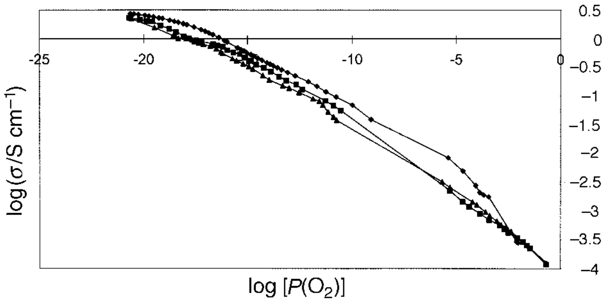

Fig. 6 Plot of $\log(\sigma/\mathrm{S\ cm^{-1}})$ *versus* $\log[P(\mathrm{O_2})]$ for porous pellets of $\mathrm{Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}}$ ($x=0.4$ ◆, 0.15 ■, 0.25 ▲)

not as great as for the Nb containing samples, $\mathrm{Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}}$ and $\mathrm{Sr_{1-y/2-3x/2}La_xTi_{1-y}Nb_yO_{3-\delta}}$ (Fig. 1–3). This resistance to re-oxidation appears to be due to slow oxygen transport, which is particularly a problem for the high Nb content samples.[2] In order to eliminate this factor and so determine the true oxygen partial pressure dependence of the conductivity, measurements were made on porous pellets (*ca.* 70% theoretical density), which were sintered at a lower temperature (950 °C rather than 1440 °C) (Fig. 5, 6). The porous pellets showed an approximate $[P(\mathrm{O_2})]^{-1/6}$ (gradient $=-0.16\pm0.02$) dependence for the $\mathrm{Sr_{1-3x/2}La_xTiO_{3-\delta}}$ samples, and an approximate $[P(\mathrm{O_2})]^{-1/4}$ (gradient $=-0.22\pm0.01$) dependence for the $\mathrm{Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}}$ samples. The problem with slow oxygen transport appears to be so great for both systems, that even in the porous samples, deviation from linearity is observed in the plots.

The plots of resistivity *vs.* temperature for the reduced samples show a linear decrease with decreasing temperature indicating that these materials are metallic. The deviation from linearity as room temperature is approached is probably a result of grain boundary effects which become more dominant as the temperature is lowered. Similar metallic character was also observed for the $\mathrm{Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}}$ system (Fig. 7).

As in the case of the $\mathrm{Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}}$ system, dense pellets of the $\mathrm{Sr_{1-y/2-3x/2}La_xTi_{1-y}Nb_yO_{3-\delta}}$ samples with both La and Nb present, showed a large resistance to re-oxidation, owing to slow oxygen transport (Fig. 2). The conductivities in reduced oxygen partial pressures were similar to the other systems studied. The presence of $\mathrm{TiO_2}$ impurity in these samples prepared with the stoichiometric amounts of reagents casts some doubt over the exact composition of the samples. A possible explanation for the $\mathrm{TiO_2}$ impurity is a result of Sr loss due to its volatility at the preparation temperatures, and potential support for this is the fact that subsequent addition of excess Sr eliminates this impurity.

Thermogravimetry indicated that all the reduced samples had oxygen contents of 2.96(1), similar to the values obtained for the $\mathrm{Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}}$ system.[2]

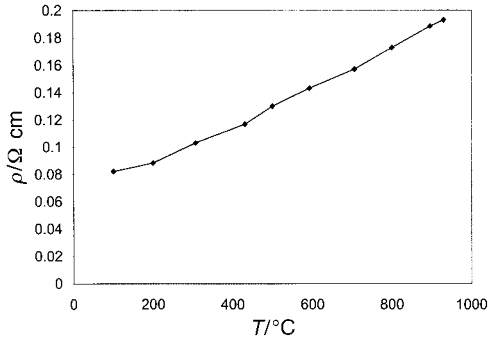

Fig. 7 Plot of resistivity *versus* temperature for $\mathrm{Sr_{0.875}Ti_{0.75}Nb_{0.25}O_{3-\delta}}$ after reduction at 930 °C

Conclusions

We have looked at three titanate based systems as potential anodes for solid oxide fuel cells: $\mathrm{Sr_{1-3x/2}La_xTiO_{3-\delta}}$, $\mathrm{Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}}$, and $\mathrm{Sr_{1-y/2-3x/2}La_xTi_{1-y}Nb_yO_{3-\delta}}$. All three systems show high conductivities in low oxygen partial pressures up to 7 S cm^{-1} [930 °C, $P(\mathrm{O_2})\approx10^{-20}$ atm], with the reduced samples exhibiting metallic conductivity. Measurements on dense samples showed a resistance to reoxidation, particularly for samples with high Nb contents. This appears to be due to slow oxygen transport, so that for the $\mathrm{Sr_{0.8}Ti_{0.6}Nb_{0.4}O_{3-\delta}}$ sample, equilibrium was far from being achieved even after keeping the sample at 930 °C in air for a week after the measurements were completed. This assumption is supported by the fact that measurements on porous samples did not show such problems and exhibited characteristic dependences, although there was still some deviation from linearity due to slow oxygen transport even in these porous samples.

The different $P(\mathrm{O_2})$ dependences of the porous La and Nb doped titanates are interesting, and require further discussion and study. The former show an approximate $[P(\mathrm{O_2})]^{-1/6}$ dependence whereas for the latter it is closer to $[P(\mathrm{O_2})]^{-1/4}$. The equation for the creation of charge carriers for the La-doped titanates can be expressed as

$$2\mathrm{Ti_{Ti}}^{\mathrm{X}}+\mathrm{O_O}^{\mathrm{X}}\overset{K_1}{\longleftrightarrow}2\mathrm{Ti_{Ti}}'+\mathrm{V_O}^{\cdot\cdot}+1/2\mathrm{O_2} \qquad (1)$$

such that,

$$[\mathrm{Ti_{Ti}}']^2=n^2=K_1\frac{[\mathrm{Ti_{Ti}}^{\mathrm{X}}]^2[\mathrm{O_O}^{\mathrm{X}}]}{[\mathrm{V_O}^{\cdot\cdot}][P(\mathrm{O_2})]^{1/2}} \qquad (2)$$

The conductivity is given by $\sigma=ne\mu$ where the mobility μ is approximately constant. The use of the simplified electroneutrality condition $[\mathrm{V_O}^{\cdot\cdot}]=1/2[\mathrm{Ti_{Ti}}']$ leads to a dependence of conductivity proportional to $[P(\mathrm{O_2})]^{-1/6}$ as observed for the La doped samples.

In the $\mathrm{Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}}$ system, there are two potential routes for the creation of electrons. Either, the reduction of $\mathrm{Ti^{4+}}$ to $\mathrm{Ti^{3+}}$, described by eqn. (1) and (2), or the reduction of $\mathrm{Nb^{5+}}$ to $\mathrm{Nb^{4+}}$, described by the following equations.

$$2\mathrm{Nb_{Ti}}^{\cdot}+\mathrm{O_O}^{\mathrm{X}}\overset{K_2}{\longleftrightarrow}2\mathrm{Nb_{Ti}}^{\mathrm{X}}+\mathrm{V_O}^{\cdot\cdot}+1/2\mathrm{O_2} \qquad (3)$$

and

$$[\mathrm{Nb_{Ti}}^{\mathrm{X}}]^2=\mathrm{K}_2\frac{[\mathrm{Nb_{Ti}}^{\cdot}][\mathrm{O_O}^{\mathrm{X}}]}{[\mathrm{V_O}^{\cdot\cdot}][P(\mathrm{O_2})]^{1/2}} \qquad (4)$$

In reducing conditions, the simplified electroneutrality equation can be written as, $1/2[\mathrm{Nb_{Ti}}^{\cdot}]+[\mathrm{V_O}^{\cdot\cdot}]=1/2[\mathrm{Ti_{Ti}}']$, which describes the concentration of vacancies present to be a function of the reduction of both titanium and niobium ions.

The stoichiometric concentration of niobium ions is substantially less than that of titanium ions. One can, therefore, envisage a situation in which the electrons formed by niobium reduction do not significantly contribute to conduction as a result of their localisation and low mobility. In addition, if the reaction in eqn. (1) proceeds to the right at higher $P(O_2)$ than reaction (3), then a certain concentration of vacancies will be present due to the formation of Nb^{4+} before the onset of titanium reduction. In this case $[V_O^{\cdot\cdot}]$ will be effectively constant in eqn. (2) for the reduction of titanium, as the total $[V_O^{\cdot\cdot}]$ present would be much greater than that just given by $1/2[Ti_{Ti}']$. A resultant $P(O_2)$ dependence of conductivity proportional to $[P(O_2)]^{-1/4}$ would be obtained in agreement with the observed result. In this respect it is noticeable for the $Sr_{1-x/2}Ti_{1-x}Nb_xO_{3-\delta}$ samples that even as prepared in air they appear grey–black, whereas for the $Sr_{1-x/2}La_xTiO_{3-\delta}$, samples the colour is only a very light grey.

It is interesting to note the metallic nature of the reduced phases. The oxygen contents of these samples determined by TGA show that only a small change in oxygen stoichiometry, $\delta \approx 0.04$, is sufficient to introduce enough Ti^{3+} to induce metallic conductivity. It would be interesting to see at which value of δ the metal–insulator transition occurs and also to examine the low-temperature electrical properties of these systems.

One of the major advantages of these materials is that they are all stable in both oxidizing and reducing conditions, with the only changes being changes in oxygen stoichiometry ($0 \leqslant \delta \leqslant 0.05$ by TG) and consequent changes in oxidation states. Thus it would be possible to easily regenerate the electrical properties of anodes made from these materials should there be a leak in the fuel cell, simply by re-reducing the sample in the fuel gas. The small changes in the unit cell with oxidation/reduction also mean that the anode is tolerant to the variation in oxygen partial pressure between fuel inlet and outlet. In addition, the fact that these samples are easily synthesised in air makes them attractive from a manufacturing cost point of view.

In order to determine the suitability for fuel cell applications further measurements need to be performed, including measurements of the thermal expansion to see if they closely match those of YSZ. Their potential use in fuel cells employing other electrolytes such as Y_2O_3/CeO_2 and $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-x}$ should also be considered. In addition catalytic studies would be profitable in order to determine the ability to internally reform CH_4.

The very low oxygen mobility observed in these titanates, indicates that these compositions do not exhibit significant mixed conductivity. To produce an effective anode material may, therefore, require the production of a composite material with a good ionic conductor such as a stabilised zirconia.

Attempts were also made to prepare similar lanthanum doped samples based on the Ruddlesden–Popper titanates, Sr_2TiO_4 and $Sr_3Ti_2O_7$, but in all cases the substitution proved unsuccessful, with perovskite impurities being observed. Similar lack of success was also encountered for Nb substitutions in the Ruddlesden–Popper phases.[2]

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