

## Electrical and microstructural characteristics of materials in the $\text{LaMnO}_{3\pm\delta}\text{--LaAlO}_3\text{--SrMnO}_{3-\delta}$ system

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### Abstract

Perovskites in the  $\text{LaMnO}_{3\pm\delta}\text{--LaAlO}_3\text{--SrMnO}_{3-\delta}$  system were studied as potential cathode materials for solid oxide fuel cells (SOFC) with regard to their microstructural and electrical characteristics, as well as their reactivity with the electrolyte. The partial exchange of lanthanum with strontium decreases electrical resistivity, while the addition of alumina increases electrical resistivity between 20 and 950°C. The chemical reactivity at the  $(\text{La}_{1-y}\text{Sr}_y)(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3/\text{YSZ}$  interface between cathode and electrolyte is negligible. © 1998 Elsevier Science S.A.

*Keywords:* Solid oxide fuel cells; Cathode;  $\text{LaMnO}_{3\pm\delta}$ ; Reactivity; Electrical resistivity

### 1. Introduction

Perovskite type oxides ( $\text{ABO}_3$ , A = La, Sr, Ca, Ba and B = Mn, Fe) are well known for their high temperature stability and wide range of electrical properties [1,2]. They have been evaluated for usage as the cathode in solid oxide fuel cells (SOFC). Among them the  $\text{LaMnO}_3$  perovskites have been studied the most extensively.

$\text{LaMnO}_3$  based materials have extremely low overpotentials for oxygen reduction at high temperatures and also have a high electronic conductivity [3,4]. The temperature expansion coefficient  $\alpha$  of  $\text{LaMnO}_3$  is close to the  $\alpha$  of the presently employed solid electrolyte YSZ (yttria stabilised cubic zirconia) ( $10.5 \times 10^{-6}/\text{K}$ ). However, the most significant limitation is the chemical reactivity between  $\text{LaMnO}_3$  and the YSZ solid electrolyte at high temperatures. During high temperature ageing lanthanum perovskites react with zirconia from the YSZ solid electrolyte forming the  $\text{La}_2\text{Zr}_2\text{O}_7$  pyrochlore phase having high electrical resistivity. Strontium for lanthanum substitution usually leads to the formation of both  $\text{La}_2\text{Zr}_2\text{O}_7$  and  $\text{SrZrO}_3$ . Increasing the strontium content hinders the formation of  $\text{La}_2\text{Zr}_2\text{O}_7$  but enhances the formation of  $\text{SrZrO}_3$  [5,6].

The incorporation of strontium influences not only the chemical compatibility but also the electrical conductivity.

It increases the electronic and ionic conductivity by the concomitant formation of  $\text{B}^{4+}$  in the  $\text{ABO}_3$  lattice and an oxygen ion vacancy. It is known that  $\text{LaAlO}_3$  based perovskites exhibit high ionic conductivity [7] and also reduce reactivity with YSZ [8].

Since chemically inert ionic and electronic conductors are considered promising as cathode materials, some perovskites with nominal compositions  $(\text{La}_{1-y}\text{Sr}_y)(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$  for  $y \leq 0.4$  and  $x \leq 0.75$  were investigated. In this work the phase compositions, microstructural and electrical characteristics, and reactivity with YSZ are reported.

### 2. Experimental

For experimental work,  $\text{La}(\text{OH})_3$  (Ventron, 99.9%),  $\text{Mn}_2\text{O}_3$  (Ventron, 99.9%),  $\text{Al}_2\text{O}_3$  (Alcoa, A-16, +99%) and  $\text{SrCO}_3$  (Ventron, 99.9%) were used. The samples were mixed, pressed into pellets and fired at 1350°C for 100 h. The compositions of the samples were  $(\text{La}_{1-y}\text{Sr}_y)(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ . For  $x = 0.3$   $y$  was 0, 0.1, 0.2, 0.3, and 0.4 and for  $y = 0.2$   $x$  was 0, 0.3, 0.5, and 0.75, i.e. eight different compositions. Fired materials were characterised by X-ray powder diffraction analysis with a Philips PW 1710 X-ray diffractometer using  $\text{Cu K}\alpha$  radiation at room temperature.

A JEOL JXA-840A scanning electron microscope (SEM) equipped with a Tracor-Northern energy dispersive X-ray analyser (EDS) was used for overall microstructural and

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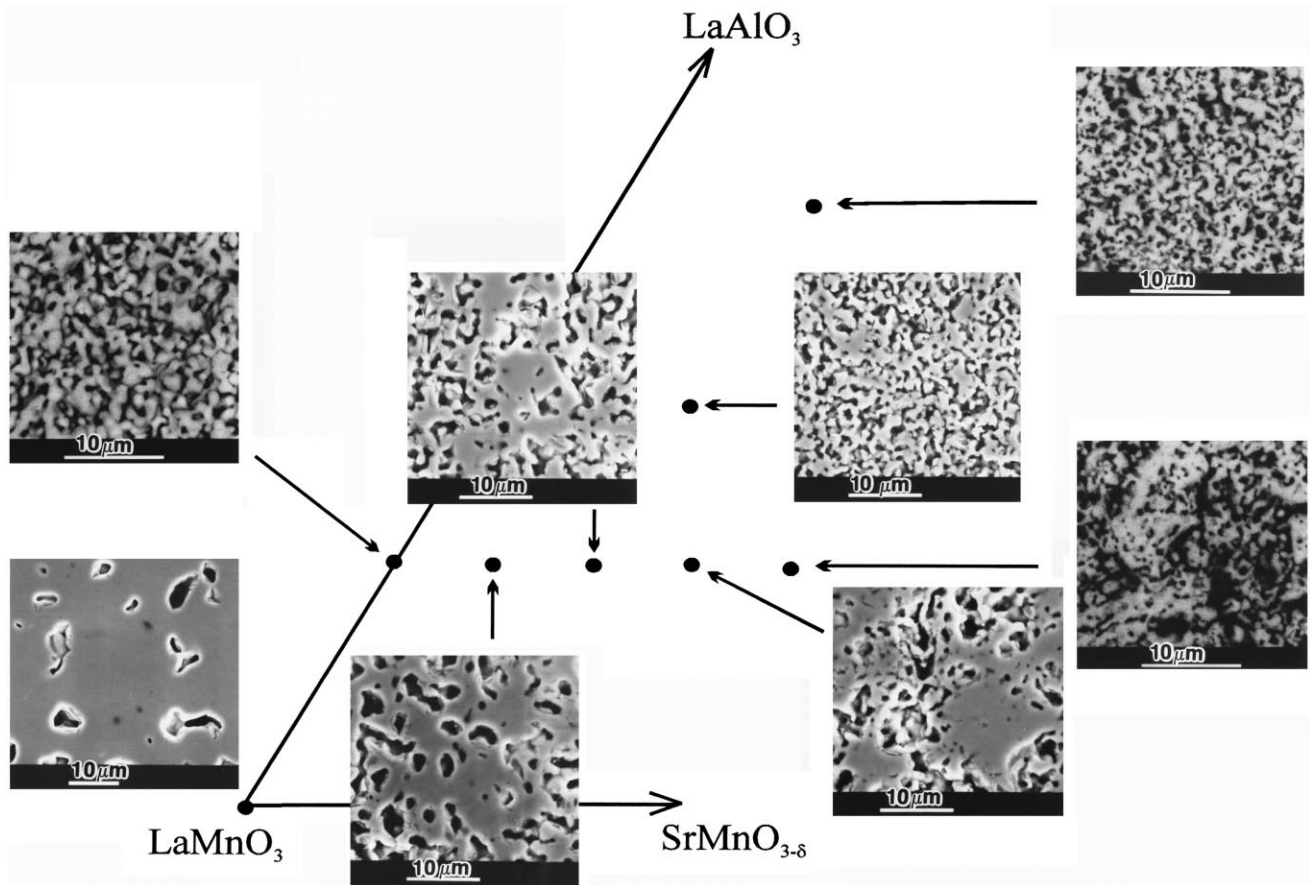


Fig. 1. Microstructures of  $(\text{La}_{1-y}\text{Sr}_y)(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$  sintered at  $1350^\circ\text{C}$ , shown schematically as part of the ternary  $\text{LaMnO}_3$ - $\text{SrMnO}_{3-\delta}$ - $\text{LaAlO}_3$  phase diagram.

compositional analysis. Samples prepared for SEM were mounted in epoxy in cross-sectional orientation and then polished using standard metallographic techniques. Prior to analysis in the SEM, the samples were coated with carbon to provide electrical conductivity and avoid charging effects.

Specific resistivities of perovskites were measured by the four-point method with a Keithley 196 multimeter and a Keithley 580 Micro-ohmmeter in the temperature range of  $20$ – $925^\circ\text{C}$  in air.

To study possible interactions with YSZ, sintered and polished pellets of YSZ and  $\text{LaMnO}_3$ ,  $\text{La}(\text{Mn}_{0.7}\text{Al}_{0.3})\text{O}_3$  and  $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Mn}_{0.7}\text{Al}_{0.3})\text{O}_3$  were hot pressed at  $1300^\circ\text{C}$  for 15 h in an alumina die. The formation of reaction products at the  $(\text{La}_{1-y}\text{Sr}_y)(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ /YSZ interface was evaluated on cross sectioned, polished samples by SEM and EDS.

### 3. Results and discussion

Microstructures of  $(\text{La}_{1-y}\text{Sr}_y)(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ , sintered at  $1350^\circ\text{C}$ , are shown schematically in Fig. 1 as a part of the ternary  $\text{LaMnO}_3$ - $\text{SrMnO}_{3-\delta}$ - $\text{LaAlO}_3$  phase diagram. Compositions in the  $\text{LaMnO}_3$  side of the phase diagram

are relatively densely sintered. The porosity increases with increasing concentration of strontium in  $(\text{La}_{1-y}\text{Sr}_y)(\text{Mn}_{0.7}\text{Al}_{0.3})\text{O}_3$ . The porosity increases and the grain size decreases with increasing concentration of aluminium in  $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ .

The logarithms of resistivity vs. reciprocal temperature for the fixed strontium content  $y = 0.2$ , i.e.  $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$  and for the fixed aluminium content  $x = 0.3$ , i.e.  $(\text{La}_{1-y}\text{Sr}_y)(\text{Mn}_{0.7}\text{Al}_{0.3})\text{O}_3$ , are shown in Figs. 2 and 3, respectively. Resistivities at room temperature and at

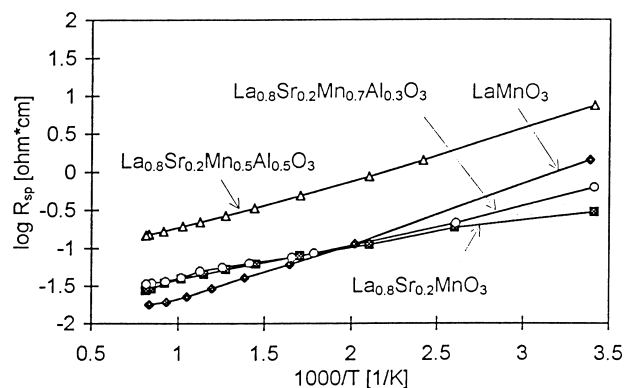


Fig. 2. The logarithms of resistivity vs. reciprocal temperature for perovskites with fixed strontium content;  $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ .

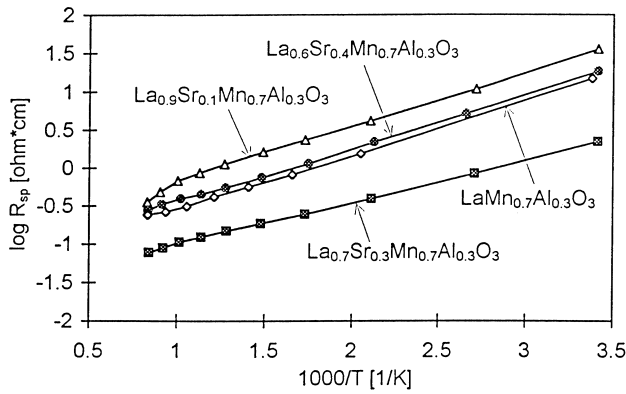


Fig. 3. The logarithms of resistivity vs. reciprocal temperature for perovskites with fixed aluminium content;  $(La_{1-y}Sr_y)(Mn_{0.7}Al_{0.3})O_3$ .

900°C are presented for different compositions, also in the ternary diagram of  $LaMnO_3$ – $SrMnO_{3-\delta}$ – $LaAlO_3$  in Fig. 4.

The specific resistivity of  $La_{0.8}Sr_{0.2}MnO_3$  at 900°C is lower than the resistivity of  $LaMnO_3$  at room temperature and slightly higher at temperatures above 200°C. The resistivities of  $(La_{0.8}Sr_{0.2})MnO_3$  and  $(La_{0.8}Sr_{0.2})(Mn_{0.7}Al_{0.3})O_3$  are nearly the same. The resistivity of  $(La_{0.8}Sr_{0.2})(Mn_{0.5}Al_{0.5})O_3$  because of its higher concentration of aluminium, is around one order of magnitude higher than that of  $LaMnO_3$ . For  $x = 0.3$ , i.e.  $(La_{1-y}Sr_y)(Mn_{0.7}Al_{0.3})O_3$ , the resistivity increases for  $y = 0.1$ , then decreases with increasing concentration of strontium up to  $y = 0.2$  by one order of magnitude and increases for higher values of  $y$ .

Microstructures of cross sectioned diffusion couples which were hot pressed at 1300°C for 15 h are shown in Fig. 5a for  $LaMnO_3/YSZ$ , in Fig. 5b for  $La(Mn_{0.7}Al_{0.3}O_{0.3})/$

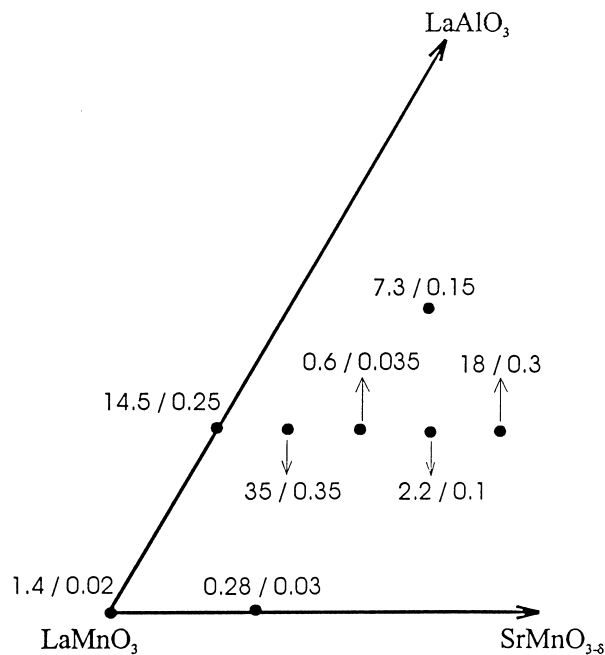


Fig. 4. Resistivities at room temperature and at 900°C ( $T_{25}/T_{900}$ ) for different compositions in the  $LaMnO_3$ – $SrMnO_{3-\delta}$ – $LaAlO_3$  diagram.

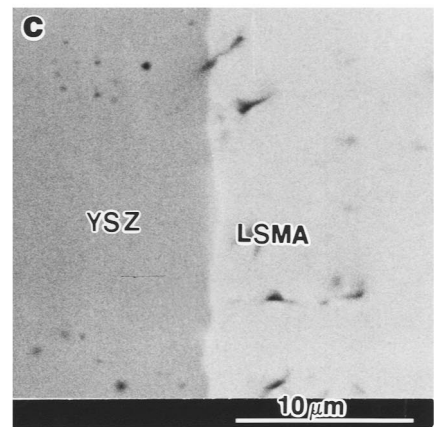
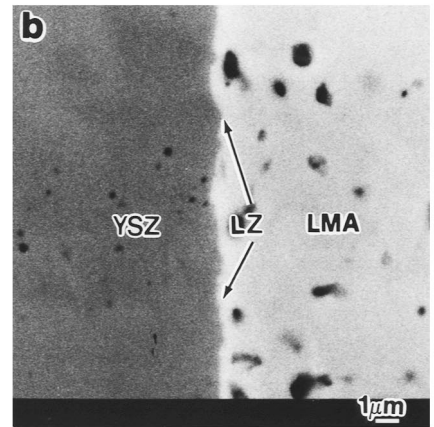
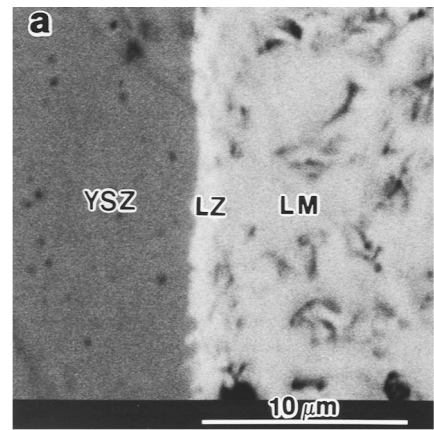


Fig. 5. Microstructure of cross sectioned diffusion couples fired at 1300°C for 15 h (LM =  $LaMnO_3$ , LMA =  $La(Mn_{0.7}Al_{0.3})O_3$ , LSMA =  $(La_{0.8}Sr_{0.2})(Mn_{0.7}Al_{0.3})O_3$ , LZ =  $La_2Zr_2O_7$ ). (a)  $LaMnO_3/YSZ$ , (b)  $La(Mn_{0.7}Al_{0.3})O_3/YSZ$ , (c)  $(La_{0.8}Sr_{0.2})(Mn_{0.7}Al_{0.3})O_3/YSZ$ .

$YSZ$  and in Fig. 5c for  $(La_{0.8}Sr_{0.2})(Mn_{0.7}Al_{0.3})O_3/YSZ$ . At the  $LaMnO_3/YSZ$  interface a layer of  $La_2Zr_2O_7$  between 2 and 3  $\mu m$  thick formed. Partial exchange of manganese with aluminium impedes the formation of  $La_2Zr_2O_7$ . A much thinner layer ( $< 1 \mu m$ ) formed at the  $La(Mn_{0.7}Al_{0.3})O_3/YSZ$  interface. In the case of  $(La_{0.8}Sr_{0.2})(Mn_{0.7}Al_{0.3})O_3/YSZ$  (Fig. 5c), no reaction product was observed at the interface. It is interesting to note that in iron based perovskites with the same composition ( $(La_{0.8}Sr_{0.2})(Fe_{0.7}Al_{0.3})O_3$ ) the reaction product was  $SrZrO_3$  [9].

#### 4. Conclusions

The microstructural and electrical characteristics of materials with nominal compositions  $(\text{La}_{1-y}\text{Sr}_y)(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$  ( $x = 0.3$  and  $y = 0, 0.1, 0.2, 0.3, 0.4$ ;  $y = 0.2$  and  $x = 0, 0.3, 0.5, 0.75$ ) prepared at  $1350^\circ\text{C}$  were evaluated. All perovskites are single phase materials. The porosity of sintered samples increases with increasing aluminium and strontium substitution.

The specific resistivity of  $(\text{La}_{1-y}\text{Sr}_y)(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ , measured from 20 to  $950^\circ\text{C}$ , increases with increasing concentration of aluminium. For  $x = 0.3$ , i.e.  $(\text{La}_{1-y}\text{Sr}_y)(\text{Mn}_{0.7}\text{Al}_{0.3})\text{O}_3$ , the resistivity increases for  $y = 0.1$  and then decreases with increasing concentration of strontium up to  $y = 0.2$  and increases for higher values of  $y$ . The reason for the higher resistivity of material with  $y = 0.1$  is not known.

Reactivity between  $(\text{La}_{1-y}\text{Sr}_y)(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$  and YSZ was studied on hot pressed diffusion couples at  $1300^\circ\text{C}$ . At the  $\text{LaMnO}_3/\text{YSZ}$  interface, a  $2\text{--}3\ \mu\text{m}$  thick film of  $\text{La}_2\text{Zr}_2\text{O}_7$  is formed. The partial exchange of manganese with aluminium suppresses the reaction rate. No reaction product was observed for strontium and aluminium doped perovskites.

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