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Chemical diffusion in perovskite cathodes of solid oxide fuel cells: the Sr doped $LaMn_{1-x}M_xO_3$ (M=Co, Fe) systems

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Abstract

This paper reports the results of chemical diffusion coefficient measurements for oxygen in $(La,Sr)(Mn,Co)O_3$ and $(La,Sr)(Mn,Fe)O_3$ using a manometric method in the temperature range of 773 to 1023 K. It was observed that the addition of Fe or Co into $(La_{4x}Sr_x)_{1-y}MnO_3$ results in a substantial increase of the chemical diffusion coefficient. In the range 25–100 mol% of Co or Fe substitution at B-site in $(La,Sr)MnO_3$, the chemical diffusion coefficient exhibits much lower activation energy than that in $(La,Sr)MnO_3$. The chemical diffusion data in $(La,Sr)(Mn,Co)O_3$ and $(La,Sr)(Mn,Fe)O_3$ system determined by the manometric method are generally in agreement with those determined by electrochemical relaxation methods reported in the literature. A comparison of the chemical diffusion data indicates that the oxygen mobility is lowest in $(La,Sr)MnO_3$ and highest in $(La,Sr)CoO_3$.

Keywords: C. Diffusion; D. Perovskite; SOFC; Sr doped $LaMn_{1-x}M_xO_3$ (M = Co, Fe)

1. Introduction

The studies on the characterisation of cathode materials such as $(La,Sr)MnO_3$ (LSM), $(La,Sr)CoO_3$ (LSC) and $(La,Sr)FeO_3$ (LSF) for solid oxide fuel cells concern mainly with their electrical and ionic conductivity properties [1–14]. These studies aim at the development of an electrode with mixed conduction that would allow efficient transfer of both charge and oxygen species. Specifically, for high performance of the cathode, it is essential that electrons are supplied at the gas/solid interface and that oxygen is transferred at a fast rate through the gas/solid interface and the electrode material. Therefore, it is important that the electrode material exhibits as high as possible both ionic and electronic conduction. On the other hand it is required that the thermal expansion coefficient of the electrode materials matches with other fuel cell components and the reactivity of the electrode with the solid electrolyte at the temperature of cell operation, which can lead to severe deterioration of its performance, is negligible [1].

LSM is a good electrode material with high electronic conductivity and thermal expansion close to that of other cell components. However, the oxygen-ion conductivity is very low which necessitates that the three phase boundary area between the electrode, electrolyte and the gas phase is maximised for the effective performance of the electrode in fuel cell operating conditions [15]. Replacement of Mn in LSM with Co and Fe results in substantially higher oxygen-ion conduction in comparison with LSM [12,13]. In this respect it would be useful to establish how the oxygen transport kinetics is modified by Co and Fe substitution into LSM at the B-site (or Mn position).

In a previous paper [16], we reported a manometric method for the determination of the chemical diffusion coefficient in oxide electrode materials and compared the chemical diffusion data for LSM with those reported

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in the literature measured by other techniques such as electrochemical relaxation methods [17]. In this manometric method, the chemical diffusion coefficient can be determined from two different approximate solutions of the Fick's second law, involving the parabolic and the logarithmic equations, which are valid at low and high values of the equilibration degree, respectively [16]. It appears that the diffusion coefficient, which in the case of these materials (LSM, LSC and LSF) is a certain measure of oxygen conduction, is sensitive to the non-stoichiometry of the material. The chemical diffusion coefficient for LSM materials exhibits different values during oxidation and reduction [16]. It also appears that the diffusion data depend on the equilibration degree and, thus the parabolic and the logarithmic equations result in different diffusion data corresponding to the non-stoichiometry range in which the applied kinetic equation is valid. Similar effect was reported for LSC [19].

The purpose of the present paper is to report the measurements of chemical diffusion coefficients in LSC, LSF and their solid solutions with LSM using the manometric method.

2. Experimental

The chemical diffusion coefficient of oxygen was measured by a manometric method. In this method the progress of the equilibration is monitored by changes in $p(O_2)$ as a function of time during oxidation and reduction experiments taking place in quasi-isobaric conditions. The experimental procedure involved evacuation of the reactor at room temperature, heating it under 1 Pa to 1070 K and then changing the temperature to the desired level. The $p(O_2)$ was isothermally increased (oxidation) or decreased (reduction) step-wise. Each increase of $p(O_2)$ resulted in a subsequent increase of oxygen consumption by the specimen. This in consequence, led to a slow decrease of $p(O_2)$ in time, Δp_t, resulting in a new equilibrium at Δp_∞,. The $p(O_2)$ change due to oxygen consumption served to monitor the equilibration degree ($\gamma = \Delta p_t / \Delta p_\infty$) as a function of time. Similar procedure was applied during the reduction experiments involving successive sudden imposition of a decreased $p(O_2)$ over an initially equilibrated specimen. Fig. 1 shows an example of the $p(O_2)$ change corresponding to successive sudden increased $p(O_2)$ (oxidation experiments) on $(La_{0.72}Sr_{0.18})(Mn_{0.75}Co_{0.25})O_{3-\delta}$ at 1109 K.

The chemical diffusion coefficient can be determined from approximate solutions of Fick's second law according to Price and Wagner [18]. For long equilibration time, corresponding to large values of the equilibration degree, γ, the logarithmic equation is applicable. For small values of the equilibration degree, the parabolic equation is applicable. Therefore, based on the equations used, one will have $D_{\log}$ and D_{par}, where the subscripts log and par denote the logarithmic and parabolic equations, respectively. The detailed procedure of the manometric method and the definitions of basic terms applied in considerations of the chemical diffusion coefficient have been described previously [16].

The oxide powders of $(La,Sr)CoO_3$, $(La,Sr)FeO_3$ and their solid solution with $(La,Sr)MnO_3$ were prepared by a wet process followed by calcination at 1000°C in air for 24 h. The calcined powders were single phase as indicated by X-ray diffraction spectra. The powder was isopressed into discs with addition of paraphine as binder and the discs were sintered at 1250°C in air for 6 h. The dimension of specimens were ~8 mm in diameter and ~3.8 mm thick. Prior to the measurements, a specimen was slowly heated (0.16 K min^{-1}) up to 773 K and then slowly cooled (0.8 K min^{-1}) to room temperature to remove any moist.

In the oxide materials studied in this work, the A-site occupancy was either 100% $[(La_{0.8}Sr_{0.2})_{10}]$ or 90% $[(La_{0.8}Sr_{0.2})_{0.9}]$ with La/Sr ratio equal to 4 in all cases. Table 1 gives the compositions and the average grain sizes estimated from SEM micrographs of oxide powders. Therefore, all the specimens reported in the present paper can be expressed by a general formula $(La_{4x}Sr_x)_{1-y}(Mn_{1-z}M_z)O_{3-\delta}$ [Mn = Co,Fe].

3. Results and discussion

3.1. Effect of sample dimensions

The determination of the chemical diffusion coefficient from the equilibration kinetic for polycrystalline specimens requires knowledge of the mechanism of the equilibration process. Specifically, it is essential to know whether the equilibration is rate controlled by the transport within individual grains or by diffusion through the entire specimen. In order to understand this, the equilibration kinetics for two different thicknesses was determined for the $(La_{0.8}Sr_{0.2})(Co_{0.75}Mn_{0.25})O_3$ specimen. Fig. 2 shows the rate constant of the equilibration process determined independently according to the parabolic and the logarithmic equations (relevant symbols are defined in Ref. [16]). As seen, in analogy to the effect of specimen thickness already observed for LSM [15], this rate constant is independent of the sample thickness. The same independence of the rate constants on the specimen thickness was also observed for LSF and LSMF materials. This indicates that the equilibration for LSC, LSF and their solid solutions with LSM is rate controlled by the diffusion through individual grains rather than by the transport through the bulk of the specimen. Consequently, a change of $p(O_2)$ in the gas phase results in

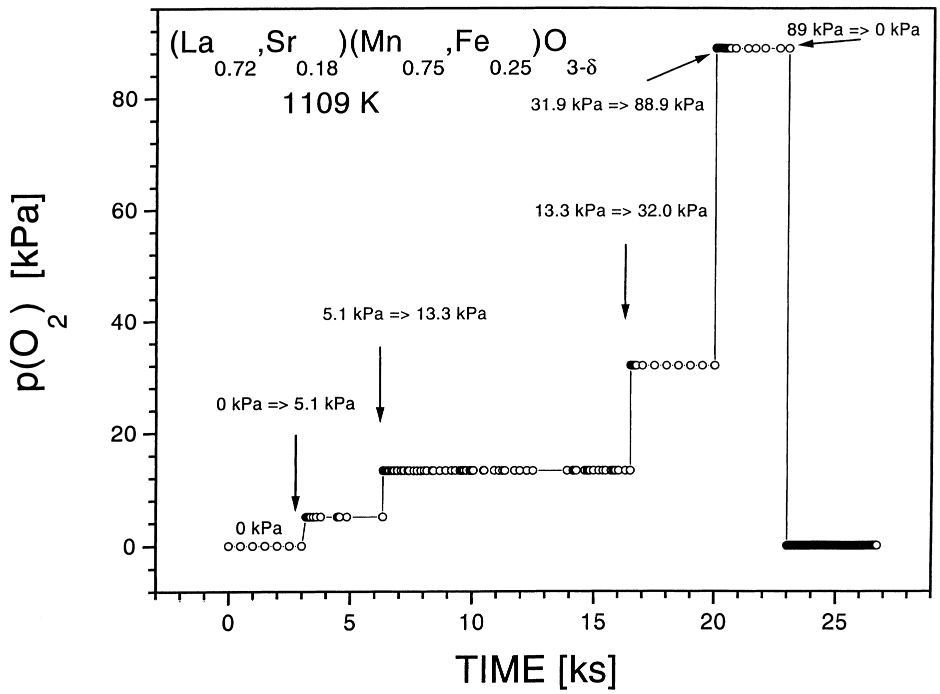

Fig. 1. The change of $p(O_2)$ corresponding to successive oxidation runs at 1109 K for $(La_{0.72}Sr_{0.18})(Mn_{0.75}Co_{0.25})O_{3-\delta}$.

Table 1
Nominal compositions of oxide powders and average grain size of the specimens as measured from SEM micrographs

Specimen	La	Sr	Co	Fe	Mn	O	Grain size (μm)
LSM	0.80	0.20	0	0	1	3	0.6
LSMC10	0.72	0.18	0.10	0	0.90	3	1.0
LSMC25	0.72	0.18	0.25	0	0.75	3	0.6
LSMC50	0.80	0.20	0.50	0	0.50	3	0.8
LSMC75	0.80	0.20	0.75	0	0.25	3	1.0
LSC	0.80	0.20	1	0	0	3	2.0
LSMF25	0.72	0.18	0	0.25	0.75	3	0.6
LSMF50	0.72	0.18	0	0.50	0.50	3	0.6
LSMF75	0.72	0.18	0	0.75	0.25	0	0.6
LSF	0.72	0.18	0	1	0	3	0.5

almost immediate imposition of the same oxygen activity along grain boundaries while equilibration of individual grains is substantially slower.

3.2. LSC

The chemical diffusion coefficients for the $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ (LSC) specimens were determined in the temperature range of 773–1100 K according to the parabolic and logarithmic equations for both oxidation and reduction runs. These data are shown in Fig. 3 along with the data reported in the literature [19,20]. As seen from the chemical diffusion coefficient data obtained in this work cover a wide temperature range (773–1023 K), the upper limit corresponding to normal

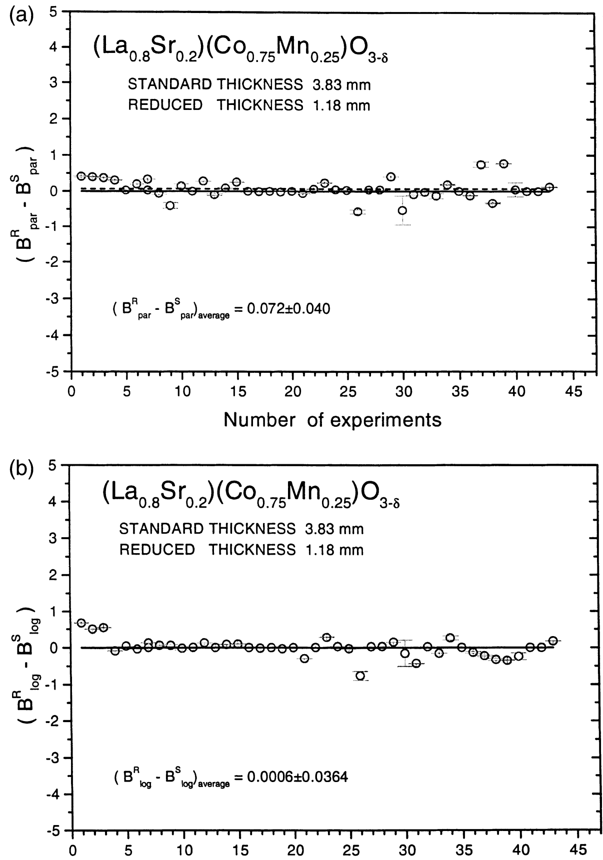

Fig. 2. The difference between the rate constant B of (a) the parabolic equation and (b) the logarithmic equation for the $(La_{0.8}Sr_{0.2})(Co_{0.75}Mn_{0.25})O_{3-\delta}$ specimens of different thickness.

operation temperature of the solid oxide fuel cell with LSC electrodes while most of the literature data [19,20] are reported for temperatures higher than 1100 K.

The diffusion data determined using the parabolic and logarithmic equations corresponds to high and low values of the equilibration degree which, respectively, correspond to the ranges $0 < \gamma < 0.5$ and $0.75 < \gamma < 0.98$. Thus the diffusion coefficient determined from oxidation kinetics using the parabolic and logarithmic equations correspond to the low and the high oxidation state of the specimen, respectively. It appears that the obtained diffusion data are sensitive to the oxidation state and, therefore, exhibit a change with equilibration degree. Similar effect was also observed by Kononchuk et al. [19].

As seen from Fig. 3, the chemical diffusion coefficient for oxidation at 1073 K, determined in this work using the logarithmic equation (high equilibration degree), is higher than that determined from reduction runs by about three orders of magnitude. This discrepancy indicates that the oxygen-ion conduction depends strongly on oxygen nonstoichiometry and the associated defect chemistry. Similar effect has been reported by Kononchuk et al. [19] who observed a strong effect of $p(O_2)$ on the chemical diffusion coefficient (Fig. 3). Moreover, Kononchuk et al. [19] have shown that the transport kinetics is different at the beginning and at the end of the equilibration process resulting in two different values of the diffusion coefficient, $D_{\text{chem-1}}$ and $D_{\text{chem-2}}$ (Fig. 3). Similar effect was observed in the present study; the diffusion coefficient determined from the parabolic and logarithmic equations, corresponding to low and high equilibration degree, respectively, assumes different values. It is interesting to note that the activation energy for oxidation is about twice larger than that for reduction (Table 2).

3.3. LSM–LSC solid solutions

Fig. 4 shows the effect of Co concentration on the chemical diffusion coefficient for LSC–LSM solid solutions at 550 and 1083 K determined from the parabolic equation for oxidation and reduction runs. Fig. 5 shows the effect of Co concentration on the chemical diffusion coefficient for LSC–LSM solid solutions at 550 and 1083 K determined from the logarithmic equation for oxidation and reduction runs. As seen the replacement of Mn in LSM with Co, resulting ultimately in the formation of LSC, does not lead to marked change in the diffusion coefficient at 1083 K. In contrast, at a lower temperature of 550 K, a substantial increase of the chemical diffusion (by 7–10 orders of magnitude) was observed due to the substitute of Mn by Co at the B-site ($y = 0.25$ or above).

Fig. 6 shows the dependence of the activation energy of the chemical diffusion coefficients on the Co

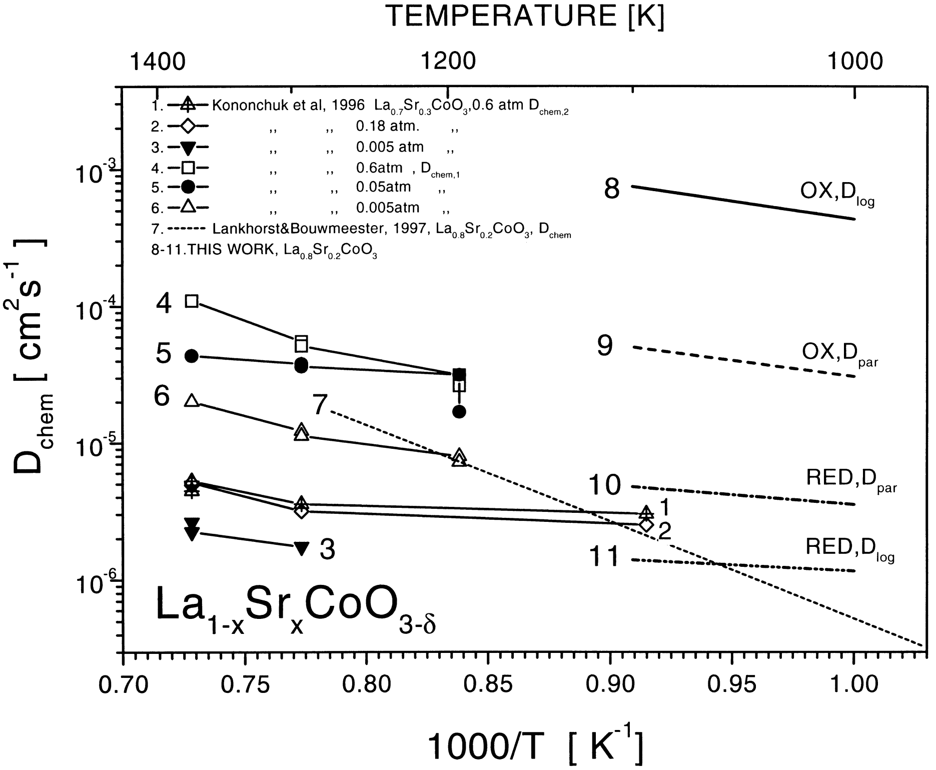

Fig. 3. Comparison of the chemical diffusion coefficient for $(La_{0.8}Sr_{0.2})CoO_{3-\delta}$ obtained on this work along with the results reported in literature.

concentration for LSC–LSM solid solutions determined from the parabolic equation for oxidation and reduction runs. Fig. 7 shows the similar plots from the logarithmic equation. As seen, addition of Co results in a drop of the activation energy from the level of 100–200 kJ mol^{-1} to almost a zero at $y=0.25$ and above. The activation energy values are given in Table 2. This effect indicates that a critical amount of the Co addition, which results in enhancement of oxygen transport kinetics, is 25%. There is little effect of Co on oxygen-ion

Table 2
Activation energy of the chemical diffusion coefficient for LSM–LSC solid solutions

No.	Specimen	Oxidation		Reduction	
		Parabolic (kJ/mol)	Logarithmic (kJ/mol)	Parabolic (kJ/mol)	Logarithmic (kJ/mol)
1	$La_{0.80}Sr_{0.20}MnO_3$	118.92±22.65	116.63±27.01	195.73±1.93	1.54.84±14.05
2	$La_{0.72}Sr_{0.18}Mn_{0.90}Co_{0.10}O_3$	98.99±44.53	184.07±14.36	222.78±11.37	186.00±15.81
3	$La_{0.72}Sr_{0.18}Mn_{0.75}Co_{0.25}O_3$	14.42±21.79	0.34±27.08	31.39±44.51	28.47±22.90
4	$La_{0.80}Sr_{0.20}Mn_{0.50}Co_{0.50}O_3$	7.51±2.53	8.99±6.92	27.44±6.54	28.83±8.10
5	$La_{0.80}Sr_{0.20}Co_{0.75}Mn_{0.25}O_3$	−10.23±7.30	−14.65±7.33	−17.35±13.08	−28.56±12.42
6	$La_{0.80}Sr_{0.20}CoO_3$	27.15±4.27	17.23±3.53	44.99±11.45	50.04±15.30

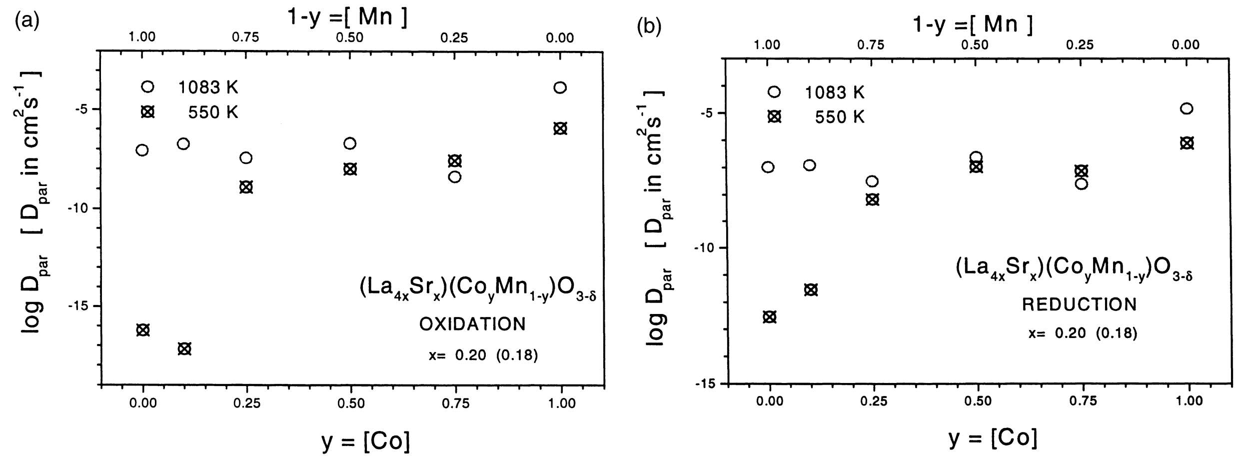

Fig. 4. The chemical diffusion coefficient, determined from the parabolic equation, for $(La_{4x}Sr_x)(Co_{1y}Mn_y)O_{3-\delta}$ as a function of Co concentration at 550 and 1083 K for (a) oxidation and (b) reduction experiments.

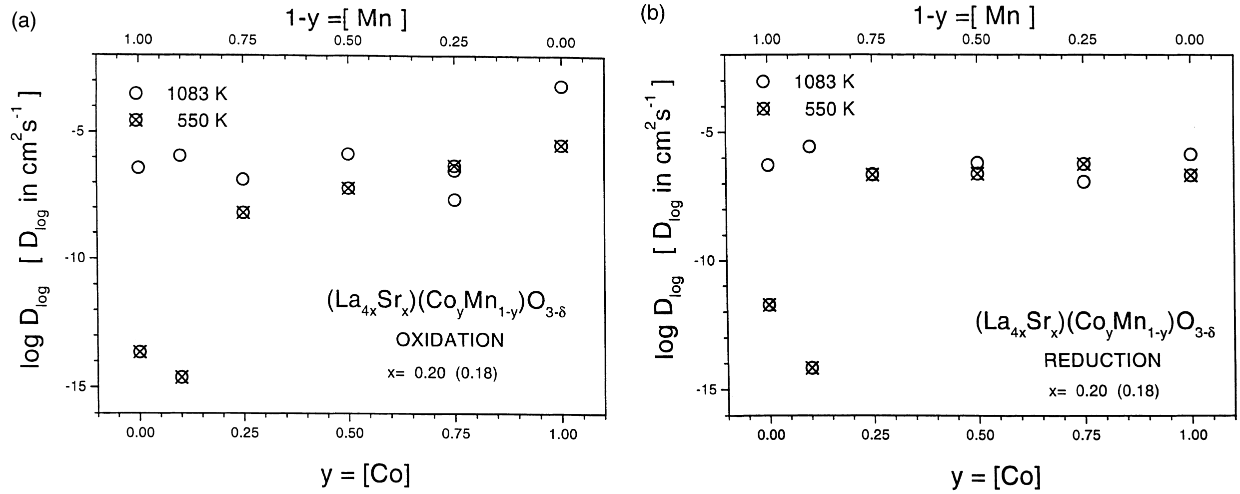

Fig. 5. The chemical diffusion coefficient, determined from the logarithmic equation, for $(La_{4x}Sr_x)(Co_{1\text{-}y}Mn_y)O_{3-\delta}$ as a function of Co concentration at 550 and 1083 K for (a) oxidation and (b) reduction experiments.

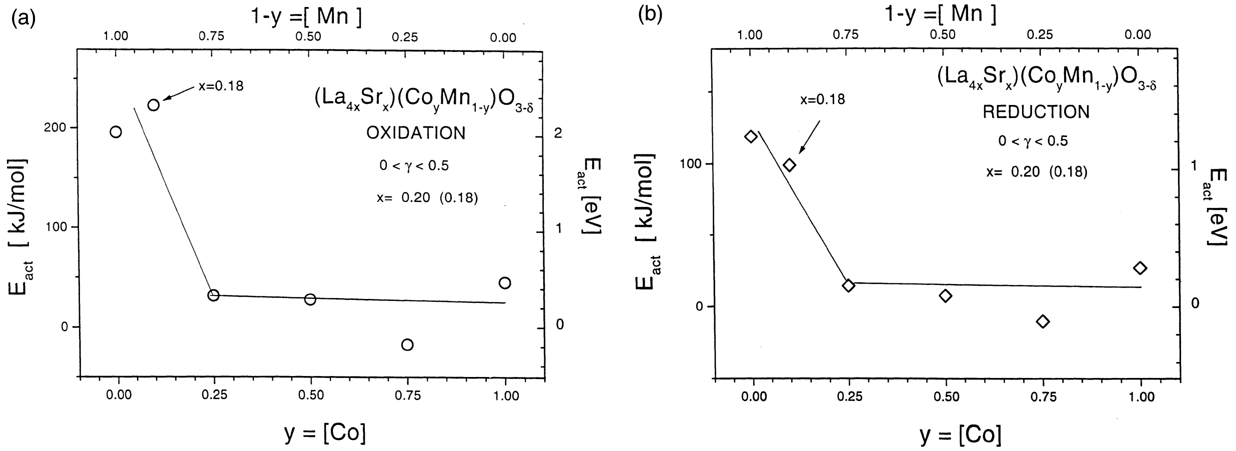

Fig. 6. The activation energy of the chemical diffusion coefficient, determined from the parabolic equation, for $(La_{4x}Sr_x)(Co_{1-y}Mn_y)O_{3-\delta}$ as a function of Co concentration for (a) oxidation and (b) reduction experiments. The lines show the trend only.

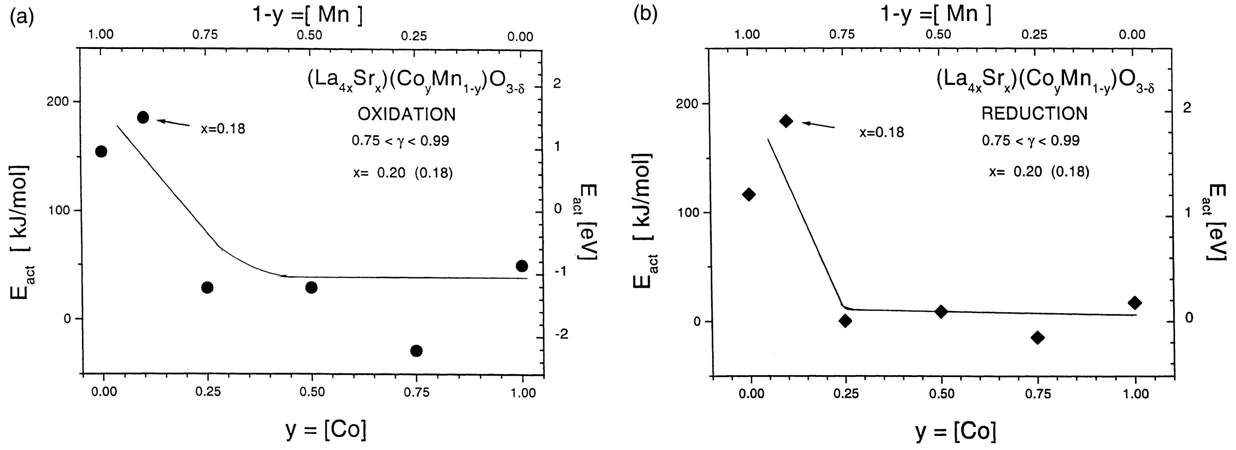

Fig. 7. The activation energy of the chemical diffusion coefficient, determined from the logarithmic equation, for $(La_{4x}Sr_x)Co_{1-y}Mn_y)$ $O_{3-\delta}$ as a function of Co concentration for (a) oxidation and (b) reduction experiments. The lines show the trend only.

conductivity of the Co-doped LSM above this concentration.

It is worth noting that the literature data indicate that substitution of more than 10% Mn at the B-site by Co, significantly reduces the stability of $(La,Sr)(CoMn)O_3$ electrodes with respect to zirconia electrolytes, thus leading to the formation of $SrZrO_3$ and La_2Zr,O_7 at the electrode/electrolyte interface at the fuel cell operating temperatures [1]. The formation of these relatively low conducting phases has a detrimental effect on the long term cell performance.

3.4. LSF

The chemical diffusion coefficient for $(La_{0.72}Sr_{0.18})$-FeO_3 (LSF) was determined in the temperature range of 773 to 1100 K. The chemical diffusion coefficient data determined in the present work was compared with those reported in the literature measured by different techniques at higher temperatures [5–7,20], as shown in Fig. 8.

The chemical diffusion coefficient for oxidation at 1073 K, determined from the logarithmic equation (high equilibration degree), is higher than that for reduction by about five orders of magnitude. Since oxidation and reduction correspond to different non-stoichiometry, the observed discrepancy indicates that non-stoichiometry has a substantial effect on oxygen conduction. This effect is markedly larger than that observed for LSC (see Fig. 3).

Elshof et al. [7] argue that at $p(O_2)$ lower than 30 Pa, the oxygen exchange process is rate controlled by a reaction at the gas/solid interface rather than by the bulk diffusion. This is not in agreement with the results obtained in this study indicating that the equilibration kinetics is rate controlled by diffusive lattice transport. However, the effect of the surface may be related to a segregation-induced diffusive resistance within the surface layer [21]. This effect may be responsible for the difference in the activation energy between oxidation and reduction experiments.

According to this model the equilibration kinetics for reduction is rate controlled by this diffusion resistance while the diffusion data obtained for oxidation seem to correspond to the bulk transport kinetics. Similar effect was observed for LSC specimens. The observed dissimilarity between reduction and oxidation kinetics may well be explained in terms of an effect of oxygen nonstoichiometry on the transport kinetics.

As seen from Fig. 8 the absolute values of the diffusion data reported in Ref. [7] are larger than those reported in this work for reduction. As also seen the diffusion data obtained in this work for LSF during oxidation exhibit exceptionally high values.

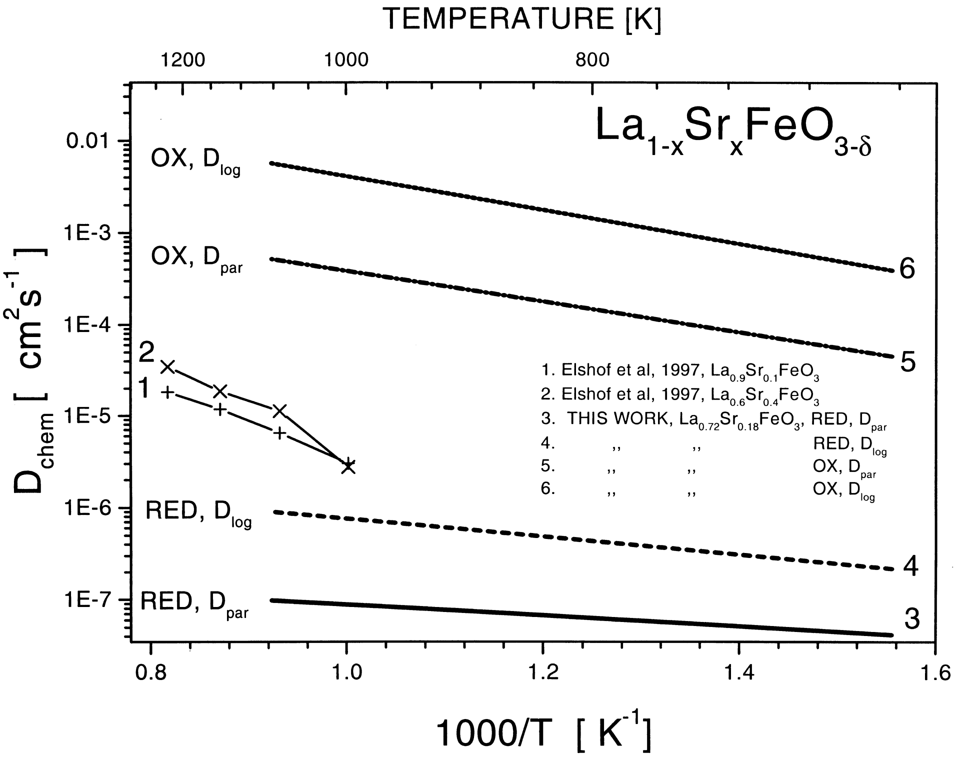

Fig. 8. Comparison of the chemical diffusion coefficient for (La$_{0.72}$Sr$_{0.18}$)FeO$_{3-\delta}$ determined according to parabolic and logarithmic equations during both oxidation and reduction experiments with literature data.

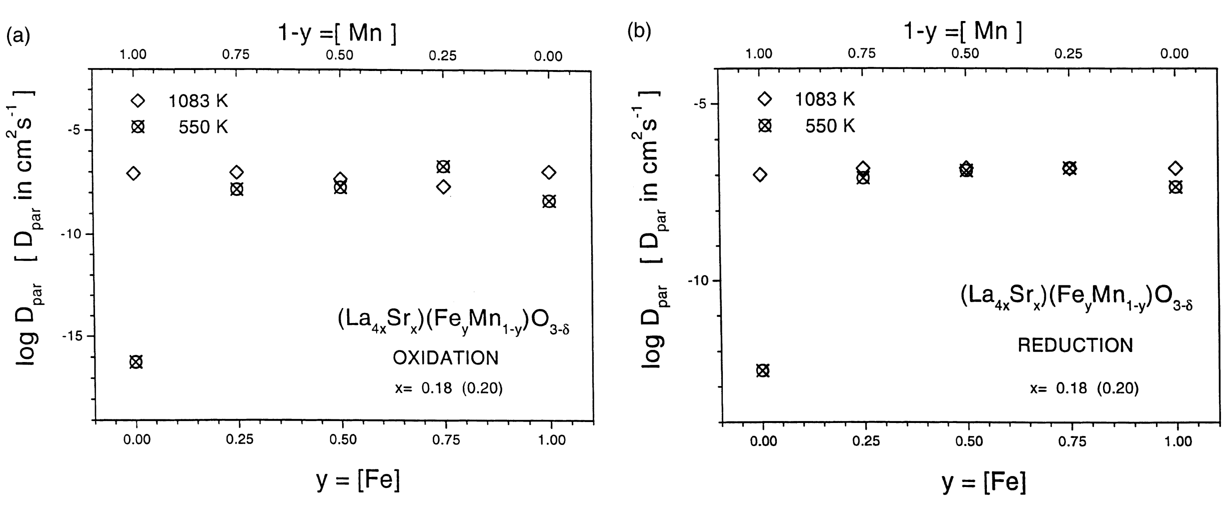

Fig. 9. The chemical diffusion coefficient, determined from the parabolic equation, for (La$_{4-x}$Sr$_x$)(Fe$_{1y}$Mn$_y$) O$_{3-\delta}$ as a function of Fe content at 550 and 1083 K for (a) oxidation and (b) reduction experiments.

3.5. LSM–LSF solid solutions

Fig. 9 illustrates the chemical diffusion coefficient for LSM–LSF solid solutions as a function of Fe concentration determined from parabolic equation during reduction and oxidation at 550 and 1083 K. Fig. 10 the data determined form the logarithmic equation. In analogy to the effect of Co substitution in LSM–LSC solid solutions, addition of Fe into (La,Sr)MnO$_3$ results in a substantial increase of the chemical diffusion coefficient by about 10 orders of magnitude at 550 K, while at 1083 K the chemical diffusion coefficient becomes almost independent of the Fe content.

The effect of Fe content on the activation energy of chemical diffusion coefficient is also similar to that of Co content in LSM–LSC solid solutions, as shown in Figs. 11 and 12. Addition of Fe results in a drop of the activation energy which assumes a close-to-zero level for both LSF and Fe-doped LSM. The activation energy values are summarised in Table 3. It is interesting to note that in analogy to the Co-doped LSM, at $y = 0.75$ of Fe, the chemical diffusion coefficient becomes practically independent of temperature.

As seen, the activation energy for undoped LSF during oxidation (E_{par} 30 kJ mol^{-1}, $E_{\text{log}} = 34$ kJ mol^{-1}) is substantially larger than that for reduction ($E_{\text{par}} =$ 11 kJ mol^{-1}, E_{log} 18 kJ mol^{-1}). This difference indicates that the same effects, considered for LSM and LSC, have an application also in this case.

3.6. Comparison of LSM, LSC and LSF

Arrhenius plots of the chemical diffusion coefficient for LSM (reported previously [16]), LSC and LSF, determined from parabolic and logarithmic equations during oxidation and reduction at different values of the

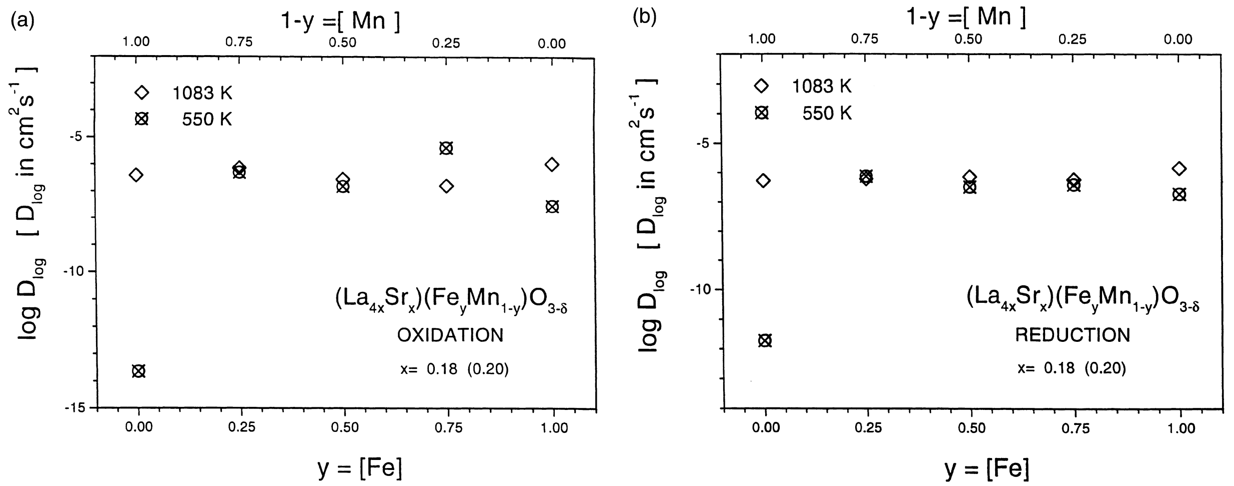

Fig. 10. The chemical diffusion coefficient, determined from the logarithmic equation, for (La$_{4-x}$Sr$_x$)(Fe$_{1y}$Mn$_y$) O$_{3-\delta}$ as a function of Fe content at 550 and 1083 K for (a) oxidation and (b) reduction experiments.

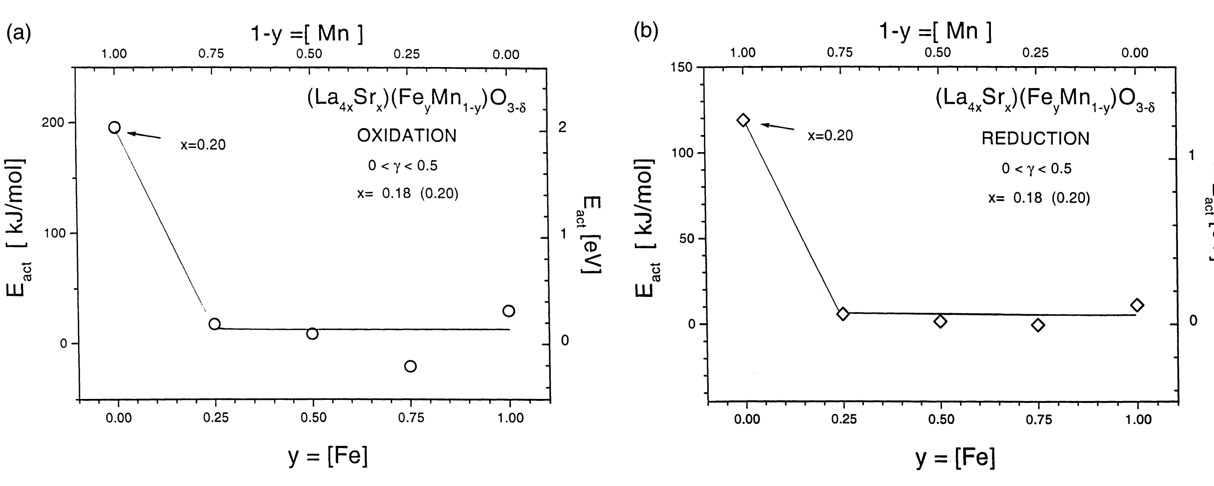

Fig. 11. The activation energy of the chemical diffusion coefficient, determined from the parabolic equation, for (La$_{4-x}$Sr$_x$)(Fe$_{1y}$Mn$_y$) O$_{3-\delta}$ as a function of Fe content for (a) oxidation and (b) reduction experiments. The lines show the trend only.

equilibration degree, are shown in Figs. 13 and 14. Comparison of these diffusion data results in the following general conclusions.

1. The diffusion data obtained during oxidation are always higher than those for reduction. The dissimilary may be explained in terms of the effect of either (i) oxygen non-stoichiometry on the kinetics or (ii) segregation-induced diffusive resistance [21].
2. In all cases the chemical diffusion coefficient for LSM is substantially lower than that for LSC and LSF, although the difference is substantially reduced at 1100 K.
3. The transport in LSC is higher than that in LSF by the factor of approximately 10.

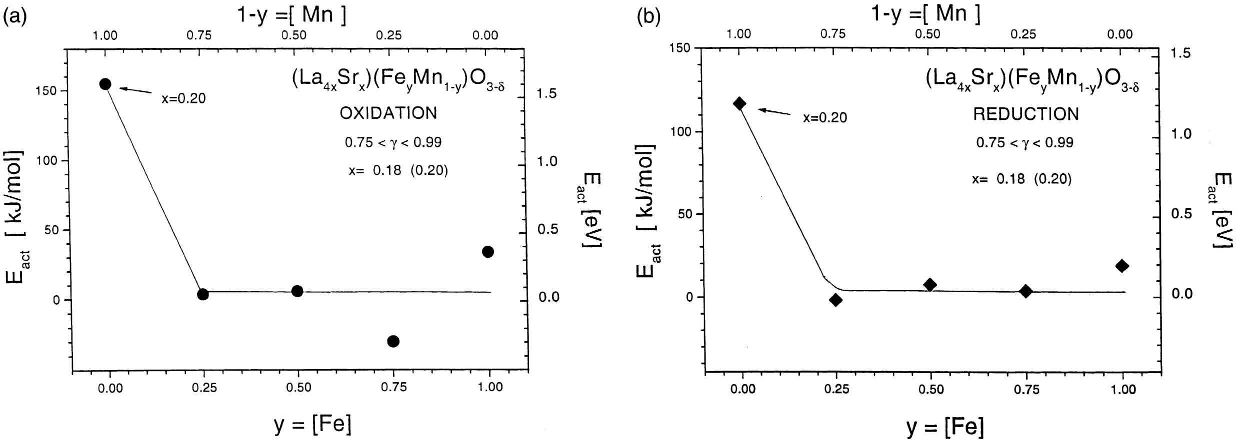

Fig. 12. The activation energy of the chemical diffusion coefficient, determined from the logarithmic equation, for $(La_{4-x}Sr_x)(Fe_{1y}Mn_y)\ O_{3-\delta}$ as a function of Fe content for (a) oxidation and (b) reduction experiments.

Table 3
Activation energy of the chemical diffusion coefficient for LSM–LSF solid solutions

No.	Specimen	Reduction		Oxidation	
		Parabolic (kJ/mol)	Logarithmic (kJ/mol)	Parabolic (kJ/mol)	Logarythmic (kJ/mol)
1	$La_{0.80}Sr_{0.20}MnO_3$	118.92±22.65	116.63±27.01	195.73±1.93	154.84±14.05
2	$La_{0.72}Sr_{0.18}Mn_{0.75}Fe_{0.25}O_3$	5.67±6.03	−1.87±4.15	17.32±6.83	3.38±6.91
3	$La_{0.72}Sr_{0.18}Fe_{0.50}Mn_{0.50}O_3$	1.55±1.56	7.38±2.01	8.47±7.48	5.76±7.25
4	$La_{0.72}Sr_{0.18}Fe_{0.75}Mn_{0.25}O_3$	−0.30±2.15	−3.75±3.07	−20.85±17.17	−30.11±15.56
5	$La_{0.72}Sr_{0.18}FeO_3$	11.24±6.80	18.47±7.37	29.63±9.34	33.74±9.74

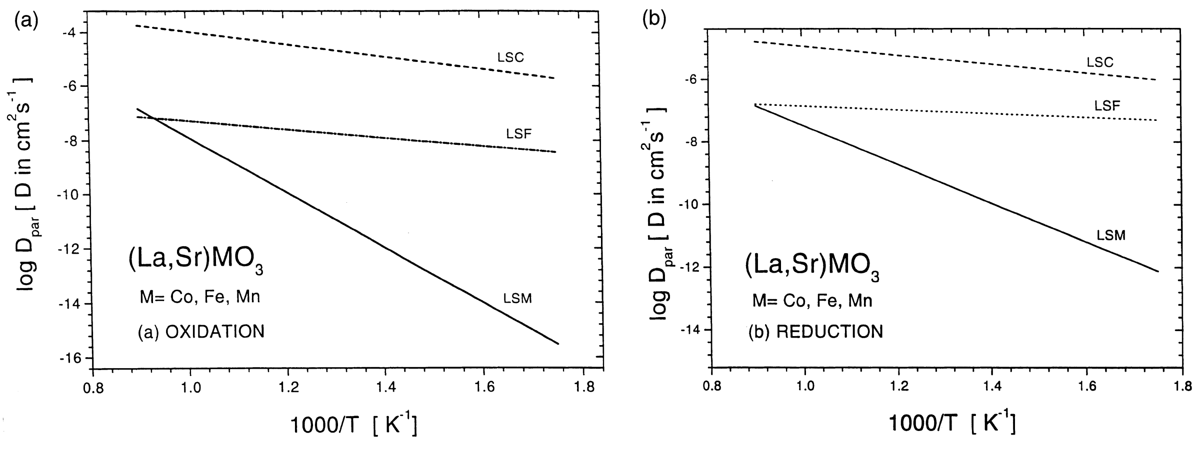

Fig. 13. The chemical diffusion coefficient as a function of reciprocal of temperature, for LSM, LSC and LSF, determined according to the parabolic equation during (a) oxidation and (b) reduction runs.

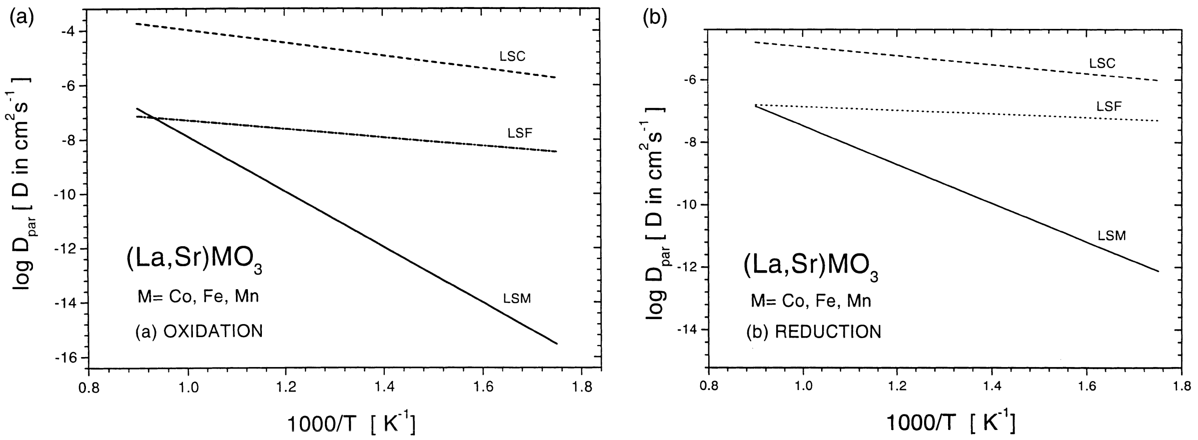

Fig. 14. The chemical diffusion coefficient as a function of reciprocal of temperature, for LSM, LSC and LSF, determined according to the logarithmic equation during (a) oxidation and (b) reduction runs.

The activation energy of the chemical diffusion coefficient assumes comparable values for both LSC and LSF, which remains in the range 10–27 kJ mol^{-1} for reduction and 30–50 kJ mol^{-1} for oxidation. The activation energy for LSM assumes substantially larger values (115–119 and 155–196 kJ mol^{-1} for oxidation and reduction, respectively), than that for LSC and LSF. In other words addition of both Co and Fe into LSM results in a substantial drop of the activation energy of the equilibration process during both reduction and oxidation.

4. Conclusions

Based on the manometric method we have determined the chemical diffusion coefficients in electrode materials LSC, LSF and their solid solutions with LSM. The diffusion coefficients for undoped LSC and LSF are substantially larger than that for LSM. Also the chemical diffusion coefficient for LSC and LSF exhibits markedly lower activation energy than that of LSM. It appears that substitution of Mn with Co or Fe in LSM above 25 mol% results in a substantial increase of oxygen mobility which is independent of temperature.

It has been shown that the equilibration mechanism of LSC and LSF and their solid solutions with LSM involves a very fast transport of oxygen along grain boundaries and substantially slower process of transport through individual grains. Thus it is possible that lowering of the grain size of the electrode materials may result in an increase of oxygen transfer through the materials.

The dissimilar kinetics for oxidation and reduction may be considered in terms of two effects:

1. The effect of oxygen nonstoichiometry, and related defects concentrations, on transport;
2. The effect of segregation-induced diffusive resistance and related electric fields on transport of charged defects [21]. Evaluation of this effect requires studies on segregation and its impact on the local transport within the segregation-induced concentration barriers would be needed to verify the effect of the surface diffusion resistance, if any.

Comparison of the diffusion data for the undoped specimens of LSM, LSC and LSF indicates that LSM is characterised by the low chemical diffusion coefficient and the high value of the activation energy while LSC and LSF exhibits the high diffusion coefficient and the low activation energy. The substantial difference in the chemical diffusion coefficient observed for LSM on one side and for both LSC and LSF on the other side may be considered in terms of the predominant defects that are responsible for ionic conduction. Namely, in the high $p(O_2)$ regime, which corresponds to the experimental conditions applied in the present study, the predominant defects in LSM are cation vacancies [13] while the transport in both LSC, LSF and their solid solutions predominantly occurs via oxygen vacancies [14] which are much faster than cation vacancies.

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