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DETERMINATION OF THE OXYGEN CHEMICAL DIFFUSION COEFFICIENT IN PEROVSKITES BY A THERMOGRAVIMETRIC METHOD

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Abstract

A thermogravimetric method has been used for the determination of the oxygen chemical diffusion coefficients in $La_{1-x}Sr_xMnO_{3+\delta}$; $x=0$; 0.05; 0.10; 0.15 (LSM).

A temperature range of 700–1000°C was studied.

The chemical diffusion coefficient varies between $1.6\cdot10^{-13}$ and $1.8\cdot10^{-10}$ cm^2 s^{-1} for the samples in the temperature range studied. The activation energy for oxygen chemical diffusion was determined to be 190–280 kJ mol^{-1} for the LSM samples. The magnitude of the chemical diffusion coefficients of the LSM samples does not depend on the strontium site occupation factor.

Keywords: diffusion, perovskite

Introduction

Strontium substituted lanthanum manganites, $La_{1-x}Sr_xMnO_{3+\delta}$ (LSM) are often used as cathodes in solid oxide fuel cells (SOFC) because of their high electrical conductivity, high catalytic activity for oxygen reduction, and chemical and mechanical stability towards the other components of the fuel cell.

The reduction of oxygen take place at or close to the triple phase boundary, where gas, electrolyte and cathode meet. It is believed that diffusion of oxygen ions in the bulk of the cathode can lead to an extension of the triple phase boundary [1, 2]. Knowledge of the oxygen diffusivity in the cathodes is therefore important in order to improve the performance of the cathode in SOFC. The oxygen diffusion coefficient can be measured by a number of methods including isotope exchange ($^{18}O/^{16}O$) (e.g. [3]) or a potentiostatic step method (e.g. [4]).

In the present work the oxygen chemical diffusion coefficient of $La_{1-x}Sr_xMnO_{3+\delta}$; $x=0$; 0.05; 0.10; 0.15 have been determined with a thermogravimetric method.

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Experimental

LSM powder samples with 0, 5, 10, and 15% of strontium substitution were prepared from the acetates in a solid state reaction as described by Krogh Andersen *et al.* [5]. The LSM powders were analysed with X-ray diffraction (XRD) (Siemens D5000) at room temperature using CuK_{α_1} radiation to confirm the formation of a single phase. The LSM powders were also analysed by scanning electron microscopy (SEM) (Jeol 100 CX TEMSCAN).

TG-measurements were performed on a SETARAM TG92-12 thermobalance. The experimental TG-equipment is shown in Fig. 1.

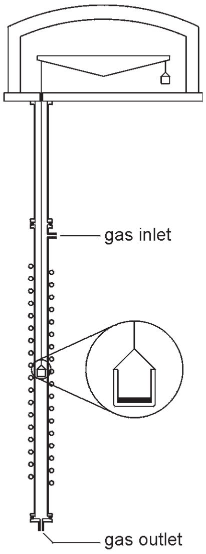

Fig. 1 Experimental set-up for the determination of the chemical diffusion coefficient and surface exchange coefficient

Approx. 50 mg of LSM powder were heated in nitrogen ($pO_2=10^{-5}$ atm) until the specimen was at equilibrium. The atmosphere was subsequently changed from nitrogen to a gas containing 50 vol% nitrogen and 50 vol% oxygen. The resulting mass change was then measured as a function of time. Isothermal measurements were performed at 700, 750, 800, 850, 900, 950 and 1000°C. Each measurement was performed more than once to estimate the experimental precision. The TG analyses were corrected for buoyancy by subtracting a blank run.

For spherical crystallites the chemical diffusion coefficient and surface exchange coefficient can be determined from [7]:

$$\frac{M_t}{M_\infty}=1-\sum_{n=1}^{\infty}6L^2\frac{\exp\left(\frac{-\beta_n^2\tilde{D}t}{a^2}\right)}{\beta_n^2\{\beta_n^2+L(L-1)\}} \qquad (1)$$

where M_t is the mass gain at time t, and M_∞ is the total mass gain. β_n is the n^{th} positive solution to $\beta_n\cot(\beta_n)+L-1=0$ and $L=ak/\tilde{D}$, where $\tilde{D}$ is the chemical diffusion coefficient, k is the surface exchange coefficient for a 1. order surface reaction, and a is the radius of the crystallites determined by XRD and SEM.

Results and discussion

The chemical diffusion coefficients and the surface exchange coefficients were determined by a TG experiment, where the oxygen partial pressure was changed from approx. 10^{-5} to 0.5 atm. Figure 2 shows the relative mass change of a thermogravimetric curve, which have been used for determination of the chemical diffusion coefficient and the surface exchange coefficient by Eq. (2).

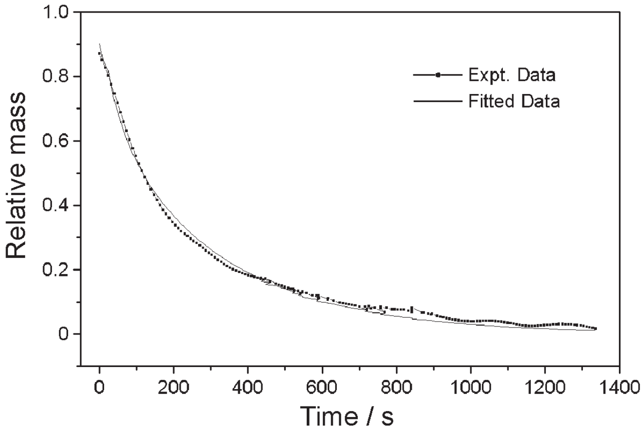

Fig. 2 The relative mass change of a thermogravimetric curve, which have been used for determination of the chemical diffusion coefficient and the surface exchange coefficient

The diffusion of the oxygen ions into the LSM crystallites could be followed, and the magnitude of $\tilde{D}$ and k could be determined from the mass change as a function of time. These parameters are governed by the defect chemistry of the perovskite, which is a function of oxygen partial pressure. Therefore, the diffusion coefficient and the surface exchange coefficient are also changed as the oxygen partial pressure is changed. The parameters, which were determined in this project, were therefore éffective parameters, as the oxygen partial pressure was varied during the experiment.

Chemical diffusion coefficient

The oxygen chemical diffusion coefficients $\tilde{D}$ for LSM5 and LSM15 are shown as a function of inverse temperature in Fig. 3. Chemical diffusion coefficients and activa-

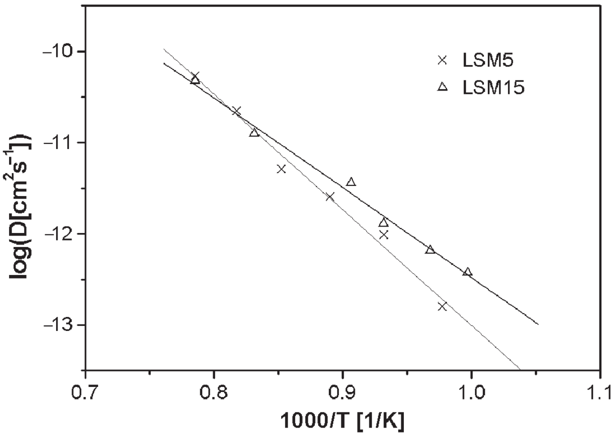

Fig. 3 Oxygen chemical diffusion coefficients for LSM5 and LSM15 as a function of inverse temperature. Lines are least squares fit to Arrhenius behaviour

tion energies for all the samples are given in Table 1. The experimental error was less than 20% for the chemical diffusion coefficient.

No particular correlation between the diffusion coefficient and the strontium site occupancy factor is seen.

There are no interstitial oxygen atoms in the perovskite lattice [8], so the diffusion of oxygen ions through the perovskite lattice is due to migration of the oxygen ion vacancies.

The oxygen incorporation in the perovskite lattice is given by reaction 2 for LSM.

$$\tfrac{1}{2}\mathrm{O}_2+\mathrm{V}_\mathrm{O}^{\bullet\bullet}+2\mathrm{Mn}_\mathrm{Mn}^\mathrm{X}\leftrightarrow\mathrm{O}_\mathrm{O}^\mathrm{X}+2\mathrm{Mn}_\mathrm{Mn}^{\bullet} \tag{2}$$

The oxygen chemical diffusion coefficient $\tilde{D}$ is related to the vacancy diffusion coefficient D_V by:

$$\tilde{D}=D_\mathrm{V}W\frac{[\mathrm{V}_\mathrm{O}^{\bullet\bullet}]}{[\mathrm{O}_\mathrm{O}^\mathrm{X}]} \tag{3}$$

where W is the thermodynamic enhancement factor, which is given by

$$W=\frac{1}{2}\frac{\partial\ln(P_{\mathrm{O}_2})}{\partial\ln(c_\mathrm{O})} \tag{4}$$

where c_O is the concentration of oxygen in the perovskite lattice.

Isothermal values of D_V are approximately constant for the $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{TmO}_3$ perovskites, Tm=Cr, Mn, Fe or Co [9]. Isothermal changes of $\tilde{D}$ as a function of strontium site fractions are therefore, according to Eq. (3), due to changes in W or in the concentration of oxygen ion vacancies.

The oxygen stoichiometry for the LSM perovskites does not vary much, as the strontium site fraction is varied, for the oxygen partial pressure examined in this project [10]. This indicates that the value of W, which is given by Eq. (4), does not change much as a function of strontium site fractions.

The substitution of lanthanum manganite by strontium on the A-site of the perovskite results either in the oxidation of manganese or the creation of oxygen ion vacancies. In LSM, manganese does get easily oxidized, and accordingly oxygen ion vacancies are not created by strontium substitution.

$$\mathrm{SrMnO_3(LaMnO_3)} \rightarrow \mathrm{Sr'_{La}} + \mathrm{Mn^{\bullet}_{Mn}} + 3\mathrm{O^X_O} \tag{5}$$

Therefore, the concentration of oxygen ion vacancies does not depend on the strontium site occupation factor.

To sum up, the value of W, D_V and the concentration of oxygen ion vacancies do not depend on the strontium site occupation factor. According to Eq. (3), this explains why the strontium site occupation factor does not have any influence on the magnitude of $\tilde{D}$. This is also observed by Berenov *et al.* [11]. The values of $\tilde{D}$ obtained in this work are also comparable with values from literature [11].

Activation energy

The chemical diffusion coefficients at 900°C and activation energies for oxygen chemical diffusion in LSM obtained in this work are listed in Table 1 together with activation energies from literature.

Table 1 Oxygen chemical diffusion coefficients at 900°C and activation energies for oxygen chemical diffusion in LSM perovskites obtained in this work and activation energies obtained by Yasuda *et al.* [12]

Sample	$\tilde{D}$/cm^2 s^{-1}	ΔH_D/kJ mol^{-1}	Yasuda *et al.* [12]
$LaMnO_{3\pm\delta}$	3.4E-11	220	–
$La_{0.95}Sr_{0.05}MnO_{3\pm\delta}$	7.3E-12	243	265
$La_{0.9}Sr_{0.1}MnO_{3\pm\delta}$	6.5E-11	279	278
$La_{0.85}Sr_{0.15}MnO_{3\pm\delta}$	9.4E-12	189	253

It is seen that activation energies estimated in this work are comparable to values obtained by Yasuda *et al.* [12]. No particular correlation between the activation energies and the strontium site occupation factor is found.

Surface exchange coefficient

The surface exchange coefficients vary between $3.9\cdot10^{-8}$ and $2\cdot10^{-6}$ cm s^{-1} for the samples in the temperature range studied. The magnitude is in fair agreement with values obtained by Berenov *et al.* [11]. The surface exchange coefficients for the samples are determined with some uncertainty. The surface reaction coefficients will often be determined with some uncertainty in materials, which exhibit a slow diffusion [13]. For these materials, the diffusion of the oxygen ions is the rate-limiting step and accordingly a minimum value of the surface exchange coefficient will be determined. The change in gas from nitrogen to 50 vol% nitrogen and 50 vol% oxygen must be fast in order to measure the surface exchange coefficient for a surface reaction. Therefore, the uncertainties in the values of the surface exchange coefficients could also to some extend have been reflected by difficulties in the gas exchange.

However, the main property of the LSM samples is the slow bulk diffusion of oxygen.

Conclusions

The thermogravimetric method is a good technique for the determination of the chemical diffusion coefficient in perovskites.

The oxygen chemical diffusion coefficients vary between $1.6\cdot10^{-13}$ and $1.8\cdot10^{-10}$ cm^2 s^{-1} for the LSM samples in the temperature range of 700–1000°C.

The content of strontium does not have any significant influence on the magnitude of the chemical diffusion coefficient of the LSM samples.

The activation energies for the oxygen chemical diffusion were determined in the range 190–280 kJ mol^{-1} for the LSM samples.

The surface exchange coefficients were measured with some uncertainty due to the slow diffusion of oxygen ions in the LSM samples.

References

1 S. B. Adler, J. A. Lane and B. C. H. Steele, J. Electrochem. Soc., 143 (1996) 3554.
2 I. Yasuda and M. Hishinuma, J. Solid State Chem., 123 (1996) 382.
3 R. A. De Souza and J. A. Kilner, Solid State Ionics, 106 (1998) 175.
4 A. Belzner, T. Gür and R. A. Huggins, Solid State Ionics, 57 (1992) 327.
5 I. G. Krogh Andersen, E. Krogh Andersen, P. Norby and E. Skou, J. Solid State Chem., 113 (1994) 320.
6 I. G. Krogh Andersen, personal communication.
7 J. Crank, The Mathematics of Diffusion, Oxford University Press, London 1975, p. 93.
8 B. C. Tofield and W. R. Scott, J. Solid State Chem., 10 (1974) 183.
9 J. Mizusaki, I. Yasuda, J. Shimoyama and F. Fueki, J. Electrochem. Soc., 140 (1993) 467.
10 H. U. Anderson, in: F. W. Poulsen, J. J. Bentzen, T. Jacobsen, E. Skou and M. J. L. Østergård (Ed.), High Temperature Electrochemical Behaviour of Fast Ion and Mixed Conductors, Proceedings of the 14th Risø International Symposium on Material Science, Risø National Laboratory 1993, p. 1.
11 A. V. Berenov, J. L. MacManus-Driscoll and J. A. Kilner, Solid State Ionics, 122 (1999) 41.
12 I. Yasuda, K. Ogasawara, M. Hishinuma, T. Kawada and M. Dokiya, Solid State Ionics, 86–88 (1996) 1197.
13 J. A. Kilner and R. A. De Souza, in: F. W. Poulsen, N. Bonanos, S. Linderoth, M. Mogensen and B. Zachau-Christiansen (Ed.), High Temperature Electrochemistry: Ceramics and Metals, Proceedings of the 17th Risø International Symposium on Material Science, Risø National Laboratory 1996, p. 41.