OXYGEN VACANCY FORMATION IN LaCrO₃ BASED PEROVSKITES

F. Boroomand, E. Wessel, L. Singheiser and K. Hilpert
Institute for Materials and Processes in Energy Systems (IWV-2)
Research Centre Jülich, 52425 Jülich, Germany

ABSTRACT

In order to elucidate the defect structure of the perovskite-type oxide solid solutions, \( \text{La}_{1-x}\text{Ca}_x\text{CrO}_3 \) (\( x=0.10 \) and \( 0.20 \)), \( \text{La}_{0.80}\text{Sr}_{0.20}\text{Cr}_{0.97}\text{V}_{0.03}\text{O}_3 \), and \( \text{LaCr}_{0.97}\text{Mg}_{0.03}\text{Al}_{0.10}\text{O}_3 \), the nonstoichiometry \( \delta \) has been measured as a function of oxygen partial pressure from 900°C to 1100°C by means of a thermogravimetric method. In addition, this technique is used for the determination of the diffusion of oxygen vacancies in \( \text{La}_{0.80}\text{Ca}_{0.20}\text{CrO}_3 \) at 1000°C. The formation of oxygen vacancies was determined for \( \text{La}_{0.90}\text{Ca}_{0.10}\text{CrO}_3 \), \( \text{La}_{0.80}\text{Sr}_{0.20}\text{Cr}_{0.97}\text{V}_{0.03}\text{O}_3 \), and \( \text{LaCr}_{0.97}\text{Mg}_{0.03}\text{Al}_{0.10}\text{O}_3 \) at 1000°C for \( pO_2=10^{-20} \) bar to \( pO_2=1 \) bar. Defect models were used to determine equilibrium constants for the formation of oxygen vacancies. Measurements between 900°C and 1100°C were carried out additionally for \( \text{La}_{0.90}\text{Ca}_{0.10}\text{CrO}_3 \) leading to enthalpy and entropy changes for the formation reaction of oxygen vacancies.

INTRODUCTION

Acceptor-doped lanthanum chromites \( \text{La}_{1-M}\text{CrO}_3 \) (\( M \): alkaline earths such as \( \text{Ca} \) and \( \text{Sr} \)) have high melting points, large electrical conductivity, and stability in reducing and oxidizing environments at high temperatures. They are used in high temperature fuel cells (SOFCs) as ceramic interconnects and as a protecting layer for metallic interconnects at operating temperatures of 800°C–1000°C.

The electronic conductivity of the stoichiometric \( \text{LaCrO}_3 \) compound is increased by substituting divalent metal ions on either the A- or B-sites of the \( \text{ABO}_3 \) lattice (1). The replacement of a trivalent ion by a divalent ion is electrically compensated by the formation of tetravalent chromium ions at high oxygen partial pressure, where the oxygen vacancy concentration has been found to be close to zero (2). By annealing in reducing atmosphere the compound loses oxygen, the charge neutrality is maintained by the formation of oxygen vacancies (2-5) and the electronic conductivity decreases with decreasing \( pO_2 \). The change in valence state of the chromium ions and the change of oxygen vacancy concentration in reducing environments leads to volume expansion (2, 6-8), which may result in mechanical stresses inside the interconnect plate in SOFCs under operating conditions.
Thermogravimetric studies of the nonstoichiometry of Sr-doped lanthanum chromites were carried out by Mizusaki et al. (3). Yasuda et al. (9) determined the defect structure of Ca-doped lanthanum chromites by electrical conductivity measurements. The present study aims to determine the oxygen nonstoichiometry \( \delta \) of \( \text{La}_{1-x}\text{Ca}_x\text{CrO}_3 \) \((x=0.10, 0.20)\), \( \text{LaCr}_{0.70}\text{Mg}_{0.05}\text{Al}_{0.15}\text{O}_3 \) (LCMA) and \( \text{La}_{0.80}\text{Sr}_{0.20}\text{Cr}_{0.97}\text{V}_{0.03}\text{O}_3 \) (LSCV) supplied by Risø National Laboratory, Denmark, by using the thermogravimetric technique. For convenience, Ca-doped lanthanum chromites are designated as LCC, followed by numbers referring to the dopant concentration, e.g. LCC10 is a \( \text{La}_{0.90}\text{Ca}_{0.10}\text{CrO}_3 \) sample. In addition, the thermogravimetric technique is used to determine the diffusion coefficient and the surface exchange coefficient of oxygen vacancies in LCC20.

**EXPERIMENTAL**

**Sample Preparation**

Powders of different substituted lanthanum chromite compositions were synthesized by solid-state reaction from the corresponding nitrates. The desired compositions were prepared by dissolving known amounts of the selected nitrates in water. The homogeneous powder mixtures were dried at 200°C and then calcined in air at 800°C for 2 h and heated to 1300°C for 12 h. For all compositions, X-ray diffraction analysis showed no second phase. The powders were pressed into pellets and sintered at 1500°C for 1 h. The chemical composition after sintering was confirmed by chemical analysis (ICP-OES).

**Thermogravimetry (TG)**

Changes in stoichiometry at elevated temperatures were studied by isothermal thermogravimetry as a function of oxygen partial pressure at temperatures of 900, 1000 and 1100°C by measuring the weight change of a given composition. Cylindrical samples of \( \text{La}_{0.80}\text{Sr}_{0.20}\text{Cr}_{0.97}\text{V}_{0.03}\text{O}_3 \) (LSCV), \( \text{LaCr}_{0.70}\text{Mg}_{0.05}\text{Al}_{0.15}\text{O}_3 \) (LCMA) and \( \text{La}_{1-x}\text{Ca}_x\text{CrO}_3 \) with \( x=0.10 \) and 0.20 of approximately 1500 mg were used for the TG measurements. The weight changes were measured to an accuracy of ±0.1 \( \mu \)g with a Mettler UMT5 balance. Different oxygen partial pressures were maintained by using the \( \text{H}_2/\text{H}_2\text{O}/\text{Ar} \) system with flow rates of about 30 ml/min and fixed by means of an electrochemical pump. The \( pO_2 \) was monitored by passing the exit gases to a calibrated oxygen sensor. Each sample was heated to the analysis temperature in an oxidizing atmosphere and allowed to equilibrate before each step change in \( pO_2 \). Diffusion experiments were conducted at 1000°C on an oxide with the composition \( \text{La}_{0.80}\text{Ca}_{0.20}\text{CrO}_3 \) with 96% of the theoretical density. The sample was 12 mm in diameter and had a thickness of 2.33 mm. At first the oxide was equilibrated in a mixture of argon and oxygen \((pO_2=10^4 \text{ bar})\) and then the \( pO_2 \) of the atmosphere was stepped down to \( 10^{20} \text{ bar} \) by changing to a mixture of \( \text{H}_2 \) and \( \text{H}_2\text{O} \). The weight change was recorded and stored every 60 s by a data acquisition system. The chemical diffusion coefficient for the oxygen vacancies and the surface exchange coefficient were determined by the diffusion model described in the next section.
THEORY

Point Defect Model

The defect chemistry of acceptor-doped lanthanum chromite has been treated by Mizusaki et al. (3) for the case of Sr-doping, and by Yasuda et al. (9) for the case of Ca-doping. Larsen et al. (10) dealt with the defect chemistry of lanthanum chromite for the case of Sr- and V-doping. Using the Kroger-Vink notation the reaction for oxygen vacancy formation can be expressed by

\[ 2 \text{Cr}^{3+} + O_0^* \leftrightarrow 2 \text{Cr}^{3+} + V_0^{**} + \frac{1}{2} O_2 (g) \]  

[1]

The equilibrium constant for the above reaction can be written as

\[ K = \frac{[\text{Cr}^{3+}_O]^2 \cdot [V_0^{**}]}{[\text{Cr}^{3+}_O]^2 \cdot [O_0^*]} \left( \frac{p(O_2)}{p_0} \right)^{\frac{1}{2}} \]  

[2]

with \( p_0 \) as standard pressure.

The condition of charge neutrality is given by

\[ [M_{La}'] = [\text{Cr}^{3+}_O] + 2[V_0^{**}] \]  

[3]

Further the B-site balance requires that

\[ [\text{Cr}^{3+}_O] + [\text{Cr}^{3+}_V] = 1 \]  

[4]

With the following definitions

\[ [M_{La}'] = x \quad : \text{amount of divalent A-site dopant (here: Ca or Sr)} \]
\[ [V_0^{**}] = \delta \quad : \text{measured as } f(pO_2) \]
\[ [O_0^*] = 3 - \delta \]

the equilibrium constant for the reduction becomes

\[ K = \frac{(2\delta - x + 1)^2 \cdot \delta}{(x - 2\delta)^2 \cdot (3 - \delta)} \left( \frac{p(O_2)}{p_0} \right)^{\frac{1}{2}} \]  

[5]

The values of \( K \) can be obtained by fitting theoretical curves to the measured data. When the standard free energy change, enthalpy change and entropy change of the defect reaction are represented by \( \Delta G^\circ \), \( \Delta H^\circ \) and \( \Delta S^\circ \), respectively, the equilibrium constant \( K \) is given by

\[ K = \exp \left( -\frac{\Delta G^\circ}{RT} \right) = \exp \left( \frac{\Delta S^\circ}{R} \right) \cdot \exp \left( -\frac{\Delta H^\circ}{RT} \right) \]  

[6]
The slope of the plot $\ln(K)$ vs. $1/T$ gives the enthalpy change and the intercept yields the entropy change for the formation of oxygen vacancies in the perovskite lattice. By using $Mg^{2+}$ as acceptor dopant and assuming that $Mg^{2+}$ enters the $LaCrO_3$ structure substitutionally for $Cr^{3+}$, the B-site balance has to be modified to

$$[Cr^3_0] + [Cr^3_0] + [Mg_{Cr}] = 1$$  \[7\]

So the equilibrium constant for the formation of oxygen vacancies becomes

$$K = \frac{(2 \delta - 2x + 1)^2 \cdot \delta}{(x - 2 \delta)^2 \cdot (3 - \delta)} \left( \frac{p(O_2)}{p_0} \right)^{1/2}$$  \[8\]

**Diffusion Model**

When $pO_2$ in the atmosphere is changed abruptly, the concentration of oxygen vacancies and $Cr^{4+}$ ions will change simultaneously towards a new equilibrium state according to equation [1]. This relaxation process comprises a surface reaction at the gas-solid interface and the diffusion of oxygen vacancies in the bulk of the solid phase. Because of the sample geometry, the transport process can be approximated by a one-dimensional model (diffusion in a plane sheet). If the diffusion coefficient $D_v$ of oxygen vacancies is concentration-independent and independent of the spatial coordinate $x$, the diffusion equation is given by

$$\frac{\partial c_v}{\partial x} = D_v \cdot \frac{\partial^2 c_v}{\partial x^2}$$  \[9\]

Under the experimental conditions mentioned above, the initial and boundary conditions are

$$c_v(x, t = 0) = c_v^0 \quad \text{for} \quad -L \leq x \leq L$$  \[10\]

$$\frac{\partial c_v}{\partial x} = 0 \quad \text{at} \quad x = 0$$  \[11\]

$$j_s = D_v \cdot \frac{\partial c_v}{\partial x} \quad \text{at} \quad x = L$$  \[12\]

Here, $c_v$ is the concentration of the diffusing species, oxygen vacancies, $D_v$ is the vacancy diffusion coefficient and $j_s$ is the particle flux density at the surface ($x=L$, $-L$). In general, the flux density at the surface is a function of the chemical potentials of oxygen in the surface of the solid and in the gas phase. The simplest reasonable assumption is that the rate of exchange is directly proportional to the difference between the actual concentration, $c_v$, of vacancies in the surface at any time and the concentration, $c_0$, which would be in equilibrium with the oxygen partial pressure in the atmosphere remote from the surface. Mathematically this means that the boundary condition at the surface is (11):
\[- D \frac{\partial c_v}{\partial x} \bigg|_{x=0} = \beta (c_0 - c_v), \quad [13]\]

where \(\beta\) is a constant of proportionality and is called surface exchange constant. The weight change as a function of time \(\Delta m(t)\), measured also by thermogravimetry, is given by integrating the particle flux density over the surface of the sample and over the time for any time step and by multiplying with the molecular weight \(M(O)\) of oxygen.

For simplicity the differential equation with the initial and boundary condition is solved by a finite difference method. The diffusion coefficient and the surface exchange coefficient are determined by fitting theoretical curves to the measured data by means of a least square minimisation of the error between measured data and calculated curve.

**RESULTS AND DISCUSSION**

**Oxygen Stoichiometry**

To check the experimental procedure, the nonstoichiometry of a sample with the composition \(La_{0.8}Sr_{0.2}Cr_{0.97}V_{0.03}O_3\), previously measured by Larsen et al. (10), was analysed. Figure 1 shows the relation between the molar oxygen deficiency \(\delta\) and the oxygen partial pressure \(pO_2\) at 1000°C. The consistency of the measured values is represented by two different measurements shown in the diagram. The calculation with \(x=0.20\) does not fit the experimental data very well. This material seems to behave like a material with a lower dopant concentration. The nonstoichiometry \(\delta\) increases with decreasing \(pO_2\) and reaches a saturation value of \(x/2=0.085\) and not of \(x/2=0.10\). The solid line in Figure 1 shows a calculation with \(x=0.17\), which is in good agreement with the experimental data. Therefore, it can be assumed that vanadium is always tetravalent and is not reduced to the trivalent state, even at low \(pO_2\). The stability of the different valence states of vanadium in the lattice of LSCV is discussed in (10). As a fit parameter, the equilibrium constant, \(K\), for the formation of oxygen vacancies was found to be \(2.3 \times 10^{-8}\).

Figure 2 shows the nonstoichiometry \(\delta\) of LCC10 as a function of oxygen partial pressure for the temperature range of 900°C-1100°C. At 1000°C the equilibrium constant was obtained to be \(1.6 \times 10^{-8}\), which is in good agreement with the data of Yasuda et al. (9) measured by electrical conductivity (see Table I). The temperature dependence of the equilibrium constant of LCC10 is shown in Figure 3. A good linearity can be seen in the plot of \(ln(K)\) vs. \(1/T\). The values of \(\Delta H^o\) and \(\Delta S^o\) are determined as 301.2 kJ/mol and 86.4 J/(K mol).
Table I. Equilibrium constant for the formation of $V_{O}^{**}$ in LCC10 for the temperature range of 900°C–1100°C

| $T$ /°C | $K$ | $K_{Lit}$ | Ref. |
|---------|-----|----------|------|
| 900     | 1.2×10^{-9} | – | – |
| 1000    | 1.63×10^{-8} | 1.88×10^{-8} | (9) |
| 1100    | 1.05×10^{-7} | – | – |

Figure 4 shows the nonstoichiometry curves of $La_{1-x}Ca_{x}CrO_{3.5}$ for the two different compositions $x=0.10$ and $0.20$ at 1000°C. The curve for the oxide with the higher dopant concentration shifts to the higher $pO_2$ range. This means that oxygen vacancies can be easily formed with increasing $x$. For $x=0.20$ the equilibrium constant was calculated as $K=2.58×10^{-8}$ which is approximately 1.6 times higher than in the case of $x=0.10$. In both cases the saturation value for the amount of nonstoichiometry is $x/2$.

The oxygen nonstoichiometry of LCMA as a function of $pO_2$ at $T=1000°C$ is shown in Figure 5. At an oxygen partial pressure of $10^{-20}$ bar the nonstoichiometry reaches a saturation value of $x/2=0.025$. The equilibrium constant for the formation of oxygen vacancies was calculated to $1.55×10^{-7}$, which is in good agreement with the data of Flandermeyer et al. (5) measured for the composition $LaCr_{0.95}Mg_{0.05}O_{3.5}$ at 1000°C. A comparison of the equilibrium constants for the different oxides is given in Table II.

Table II. Equilibrium constants for the formation of $V_{O}^{**}$ in lanthanum chromite based perovskites at 1000°C

| composition | divalent cation | $x$ | $K$ (present study) | $K_{Lit}$ (present study) | Ref. |
|-------------|-----------------|-----|---------------------|--------------------------|------|
| $LaCr_{0.79}Mg_{0.05}Al_{0.10}O_{3.5}$ | Mg | 5 | $1.55×10^{-7}$ | – | – |
| $LaCr_{0.95}Mg_{0.05}O_{3.5}$ | Mg | 5 | – | $1.77×10^{-7}$ | (5) |
| $LaCr_{0.95}Mg_{0.05}O_{3.5}$ | Mg | 5 | – | $1.45×10^{-7}$ | (4) |
| $La_{0.90}Ca_{0.10}O_{3.5}$ | Ca | 10 | $1.63×10^{-8}$ | $1.88×10^{-8}$ | (9) |
| $La_{0.80}Sr_{0.20}Cr_{0.97}V_{0.03}O_{3.5}$ | Sr / V | 20 / 3 | $2.29×10^{-8}$ | $1.78×10^{-9}$ | (10) |
| $La_{0.80}Ca_{0.20}CrO_{3.5}$ | Ca | 20 | $2.58×10^{-8}$ | – | – |

Diffusion Measurement

For the composition $La_{0.8}Ca_{0.2}CrO_{3.5}$ (LCC20) diffusion measurements were carried out at a temperature of 1000°C. Figure 6 shows a typical time change of weight by the release of oxygen from LCC20 at 1000°C after the fast decrease of $pO_2$ from $10^{-4}$ bar to $10^{-20}$ bar. The theoretical curve (solid line) computed by using the diffusion model discussed in the previous section agrees well with the observed data, demonstrating that the relaxation behaviour is well interpreted in terms of an oxygen vacancy diffusion
process in the solid which is partially controlled by surface reaction. The diffusion coefficient of oxygen vacancies was found to be $D_v = 8.44 \times 10^{-8}$ cm$^2$/s and the surface exchange coefficient $\beta = 4.62 \times 10^{-5}$ cm/s. The determined values are comparable to those of other mixed-conducting perovskite type oxides given in Table III.

| Ref.           | Method           | $D_v$ /cm$^2$·s$^{-1}$ | $\beta$ /cm·s$^{-1}$ |
|----------------|------------------|------------------------|-----------------------|
| present study  | thermogravimetry | 8.44X10$^{-8}$         | 4.62X10$^{-5}$        |
| Sakai et al. (12) | elektrochem. cell | 1.0X10$^{-7}$         | 1.2X10$^{-5}$        |
| Sakai et al. (13) | elektrochem. cell | 3.0X10$^{-6}$         |                        |
| Sakai et al. (12) | elektrochem. cell | 7.0X10$^{-5}$         |                        |
| Yasuda et al. (14) | elektr. conductivity | 7.94X10$^{-6}$        |                        |

$^{a)}$ : $La_{0.96}Ca_{0.10}CrO_3.8$ sample with $K=1.88X10^{-8}$
$^{b)}$ : $La_{0.70}Ca_{0.30}CrO_3.8$ sample with $K=1.37X10^{-7}$
$^{c)}$ : $La_{0.75}Ca_{0.25}CrO_3.8$ sample with $K=3.22X10^{-8}$

### CONCLUSIONS

In thermogravimetric experiments on acceptor-doped lanthanum chromites in different environments the following conclusions can be drawn.

The TG data of Riso sample LSCV show at low $pO_2$ some deviation from the defect model of a perovskite specimen doped with 20% on A-site. Nonstoichiometry data measurements show that in the LSCV lattice vanadium is always tetravalent, even under reducing conditions. Therefore, this specimen behaves like a sample with a 17% dopant concentration on the A site. The nonstoichiometry $\delta$ of the perovskite-type oxide solid solution LCC10 was measured as a function of oxygen partial pressure $pO_2$ for the temperature range of 900°C–1100°C. Thermodynamic data for the formation of oxygen vacancies were calculated. The equilibrium constant at 1000°C was in good agreement with the data determined by Yasuda and Hikita (9). Comparing the two Ca concentrations of 10% and 20% the nonstoichiometry $\delta$ reaches asymptotically a saturation value of $x/2$. The equilibrium constant increases with increasing $x$, which means oxygen vacancies can be easily formed. TG measurements on LCMA show that the nonstoichiometry can be well interpreted by the defect model for B site substitution. The comparison of the equilibrium constant for the formation of vacancies with the data of Flandermeyer et al. (5), measured for $LaCr_{0.95}Mg_{0.05}O_3.8$ shows that the Al in LCMA does not have a significant influence on the defect structure of the oxide.

The oxygen vacancy diffusion coefficient and the surface exchange coefficient was determined for the first time by thermogravimetry for the solid state solution LCC20.
at 1000°C and was comparable to those of other mixed-conducting perovskite type oxides.

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Fig. 1. Nonstoichiometry of $La_{0.85}Sr_{0.15}Cr_{0.97}V_{0.03}O_3$ sample (Riso) at 1000°C as a function of $pO_2$.

Fig. 2. Nonstoichiometry of $La_{0.95}Ca_{0.05}CrO_3$ for the temperature range of 900°C-1100°C as a function of $pO_2$. 

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Fig. 3. Temperature dependence of the equilibrium constant of the defect reaction for $La_{0.90}Ca_{0.10}CrO_3.8$.

\[ \text{Fit: } \Delta H^\circ = 301.2 \text{ kJ/mol} \]
\[ \Delta S^\circ = 86.4 \text{ J/(K mol)} \]

Fig. 4. Nonstoichiometry of $La_{x}Ca_xCrO_3.5$ at 1000°C as a function of $pO_2$ for $x=0.10$ and 0.20.
Fig. 5. Nonstoichiometry of LaCr$_{0.79}$Mg$_{0.02}$Al$_{0.16}$O$_{3.8}$ sample at 1000°C as a function of $pO_2$.

Fig. 6. Time dependence of weight loss by the release of oxygen from LCC20 at 1000°C after the fast decrease of $pO_2$ from $10^4$ bar to $10^{20}$ bar.

- $D_v = 8.44 \times 10^8$ cm$^2$/s
- $\beta = 4.62 \times 10^5$ cm/s
- $d = 2.33$ mm, $\rho = 95.2\%$ of theoretical dense

- measurement
- fit