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Nonstoichiometry and Relaxation Kinetics of Nanocrystalline Mixed Praseodymium–Cerium Oxide $Pr_{0\cdot7}Ce_{0\cdot3}O_{2-x}$

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Abstract

The oxygen deficiency and kinetics of oxygen uptake and release of nanocrystalline mixed praseodymium–cerium oxide with composition $Pr_{0\cdot7}Ce_{0\cdot3}O_{2-x}$ *were investigated by combining coulometric titration and potentiometric measurements using stabilised zirconia oxygen concentration cells. The* $P(O_2)$ *versus composition isotherms indicate a two-phase region at high* $P(O_2)$ $[P(O_2) > 0\cdot1$ *bar at 560°C] and a single-phase region at lower* $P(O_2)$*. The oxygen pressure dependence in the homogeneous region can be described by a power law with an exponent* $(-1/6)$*, in accordance with doubly charged oxygen vacancies as majority defects. The enthalpy of reduction amounts to* $(2\cdot9 \pm 0\cdot3)$ *eV. The chemical diffusion coefficients are of the order of* $10^{-6}\,cm^2\,s^{-1}$ *at 640°C with an activation energy of* $\approx 0\cdot3$ *eV. The low activation energy for diffusion may be related to the high density of interface sites in the nanocrystalline material. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: defects, interfaces, diffusion, rare earth metal oxides, nonstoichiometry.

1 Introduction

Oxygen storage materials help regulate the air-to-fuel ratio leading to more effective operation of catalytic converters in automobiles.[1] The oxygen storage capacity of an oxide is related to its range of nonstoichiometry and, therefore, to the valence change of the cation. Mixed praseodymium–cerium oxides have an exceptionally high oxygen storage capacity, because the valence change of the praseodymium cation (Pr^{4+}/Pr^{3+}) is particularly easy. For this reason, it is interesting to study the oxygen deficiency of these compounds and their relaxation kinetics after chemical or electrochemical polarization experiments. Several investigators studied the phase relations, crystal structure and ionic transference number of mixed $Pr_yCe_{1-y}O_{2-x}$.[2–6] The oxygen deficiency and electrical conductivity of a mixed oxide with composition $Pr_{0\cdot55}Ce_{0\cdot45}O_{2-x}$ was previously investigated in our laboratory.[7]

Nanocrystalline materials are the subject of much interest in recent years, given the expectation that the high density of interfaces could lead to significant modifications in defect and transport properties of these materials. For example, nanocrystalline compounds seem to exhibit enhanced non-stoichiometry, because of the greater number of interface sites where defect formation energies are reduced.[8] Furthermore, one expects an increase of diffusive transport at and near interfaces, which are regions of high defect density and mobility.[9] Consequently, we expect the nanocrystalline material to exhibit a higher oxygen storage capacity and also a faster response to changes of the oxygen partial pressure in the gas phase. Both features are definitely of interest for technological applications.

In this work, we present experimental data for the oxygen deficiency of nanocrystalline praseodymium–cerium oxide $Pr_{0\cdot7}Ce_{0\cdot3}O_{2-x}$ and for the equilibration kinetics using yttria-stabilised zirconia oxygen concentration cells. The composition of the oxide is modified by coulometric titration while the dependence of the oxygen partial pressure on the non-stoichiometry x is deduced from the steady state voltage across the zirconia electrolyte. The time dependence of the potential following a titration step provides information about transient phenomena in these materials.

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2 Theory

2.1 Coulometric titration

A current through the galvanic cell, $Pr_{0\cdot7}Ce_{0\cdot3}$-O_{2-x}|Pt|Y-ZrO_2|O_2(air)|Pt, changes the composition of the oxide according to Faraday's law. The amount of electrolyzed oxygen $\Delta n(O_2)$ was calculated from the current I and the time t (F: Faraday's constant) according to:

$$\Delta n(O_2) = It/4F + \left(P_f - P_i\right)V/RT \qquad (1)$$

The right-hand side of this equation takes into account the so-called dead-volume correction: P_f and P_i are the final and the initial oxygen partial pressures, respectively, and V/RT is the dead-volume coefficient. The time integral of the current is a very precise measure of the concentration variation. After a certain amount of current has been passed, the equilibrium open circuit voltage is determined. The integration of coulometric titration curves gives the thermodynamic quantities as a function of composition with high resolution.[10]

We consider mixed praseodymium-cerium oxide as a pseudo-binary system, because the Pr/Ce ratio does not change during the measurements. The phase rule shows that thermodynamic activities are independent of composition as long as two phases are in equilibrium with each other. Changes in the relative amounts of the two phases do not modify the activities of the components and therefore maintain the cell voltage constant. This creates voltage plateaus in regions of two-phase equilibrium and provides means for determining the limits of nonstoichiometry of given phases.

2.2 Relaxation measurements

Measurements of the time dependence of the cell voltage after a titration step are a powerful technique to investigate the kinetics of oxygen uptake and release in materials. After a constant current is applied for a certain time, the current flow is interrupted and during the following relaxation process, the time dependence of the voltage can be related to oxygen exchange at the interface gas/electrode and to chemical diffusion in the electrode.

Assuming that the rate-limiting step is the transport process in the solid, solutions exist for the concentration of the mobile species as a function of time.[11–13] One can distinguish short-time and long-time solutions, depending on the thickness of the sample L and the chemical diffusion coefficient D. In an oxygen-deficient oxide, like praseodymium–cerium oxide, a change in oxygen partial pressure produces an oxygen vacancy excess or deficit at the surface. The vacancies then diffuse into or out of the solid to regain thermodynamic equilibrium. We are thus considering a chemical diffusion process, characterized by the diffusivity of oxygen vacancies D_O and electrons D_e. According to Darken's equation, the chemical diffusion coefficient in a mixed ionic-electronic conductor is:[14]

$$D = t_e D_O + t_O D_e \qquad (2)$$

where t_e and t_O are the transference number of electrons and oxygen ions, respectively. In $Pr_{0\cdot7}Ce_{0\cdot3}O_{2-x}$ an ionic transference number $t_O = 0{\cdot}11$ is reported.[2] If the oxide sample is compact and non-porous, we can consider that we have diffusion from a constant source into a finite solid and we can solve Fick's second equation with the following boundary conditions:

$c = c_0$ at $t = 0$ for $0 < x < L$
(uniform initial concentration)

$c = c_1$ at $t = \infty$ for $0 < x < L$
(uniform final concentration)

$c = c_1$ at $t > 0$ for $x = L$
(constant surface concentration)

Here t is the time variable, x the distance parameter, the subscripts 0 and 1 indicate the initial and final states. The resulting solution for long times, $Dt/L^2 > 0{\cdot}3$, is:[11]

$$(c - c_0)/(c_1 - c_0) = 1 - \left(8/\pi^2\right)\exp\left(-D\pi^2 t/L^2\right) \qquad (3)$$

The concentration variation $(c_1 - c_0)$ is directly related to the amount of charge passed through the cell. The chemical diffusion coefficient D may be calculated from the time dependence of the cell voltage E by a plot ln $[E(t) - E(\infty)]$ versus t, which, at long times, yields a straight line with absolute slope $(D\pi^2/L^2)$.[12,13]

For short times, $Dt << L^2$, the concentration ratio $(c - c_0)/(c_1 - c_0)$ is proportional to the square root of time:[11]

$$(c - c_0)/(c_1 - c_0) = 4\left(Dt/\pi L^2\right)^{1/2} \qquad (4)$$

Consequently, the chemical diffusion coefficient D can be calculated from the slope of the straight line $(c - c_0)/(c_1 - c_0)$ versus $t^{1/2}$. A consistency test is to compare values for D obtained from short-time and long-time solutions.

3 Experimental

The mixed oxide was prepared by coprecipitation of cerium nitrate and praseodymium nitrate with oxalic acid solutions. The precipitates were calcined 6 h at 650°C and 2 h at 750°C.[7] The composition of the oxide was investigated by iodometric titration. These measurements confirmed that cerium is valence-invariant and remains largely in the Ce^{4+} state.[10]

All X-ray diffraction peaks were found to correspond to a single phase: the solid solution retains the fluorite structure of the β-praseodymium oxide Pr_6O_{11} even with 30 mol% cerium oxide in contrast to conventional polycrystalline praseodymium–cerium oxides, which are generally composed of two phases.[4,5] An enhanced solubility in nanocrystalline materials, due to solute segregation at the intergranular boundaries, is theoretically expected and was experimentally observed, e.g. in copper-doped cerium dioxide.[15] An average grain size of 35 nm was estimated from line broadening.

A double stabilised zirconia cell with platinum paste electrodes was used for the coulometric and potentiometric measurements (galvanostat EG&G 362, multimeter Keithley 197). The current direction was regularly reversed in order to check possible hysteresis effects. The equilibrium potential was taken when the value did not change more than 0·1 mV during 1 h. Reversibility tests were performed by applying a small current to the cell ($<1\,\mu$A, 10 s) and recording the transient of the open-circuit potential after the current flow. The absence of gas leakage was checked by long-time measurements of the cell voltage.[10]

4 Results

Figure 1 shows isotherms of oxygen deficiency $(x - x_0)$ versus oxygen partial pressure for $Pr_{0{\cdot}7}Ce_{0{\cdot}3}O_{2-x}$ at 640, 560 and 470°C. The oxygen deficiency x is indicated with respect to the unknown value x_0 corresponding to the initial equilibrium in air. A steep change of oxygen pressure with composition is observed around $(x - x_0) = 0{\cdot}1$, probably corresponding to a single-phase region. A plateau region seems to exist at small $(x - x_0)$ and high oxygen partial pressures, where two phases may coexist. The characteristic exponent is calculated according to:

$$\log\ x = A - \log\ P(O_2)/n \tag{5}$$

The value of n is approximately 6 at 560 and 640°C and 3 at 470°C.

Figures 2 and 3 present the evaluation of chemical diffusion coefficients at 640°C from the time dependence of the cell potential after a coulometric titration step using the short time approximation (Fig. 2: $D = 1{\cdot}5\ 10^{-6}\,cm^2\,s^{-1}$) and the long-time approximation (Fig. 3: $D = 1{\cdot}1\,10^{-6}\,cm^2\,s^{-1}$). The values of D calculated from eqns (3) and (4) are compatible. In Fig. 4, chemical diffusion coefficients at 640 and 560°C are shown as a function of the oxygen deficiency of the oxide. As the

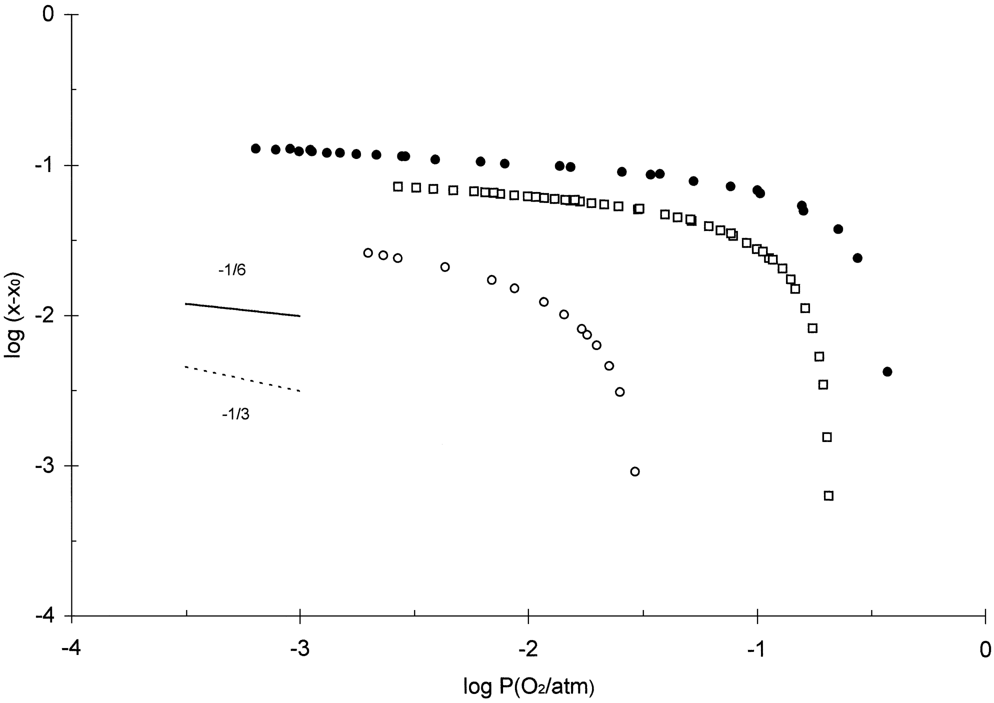

Fig. 1. Oxygen deficiency as a function of oxygen partial pressure for $Pr_{0{\cdot}7}Ce_{0{\cdot}3}O_{2-x}$, (●: 640°C, □: 560°C, ○: 470°C).

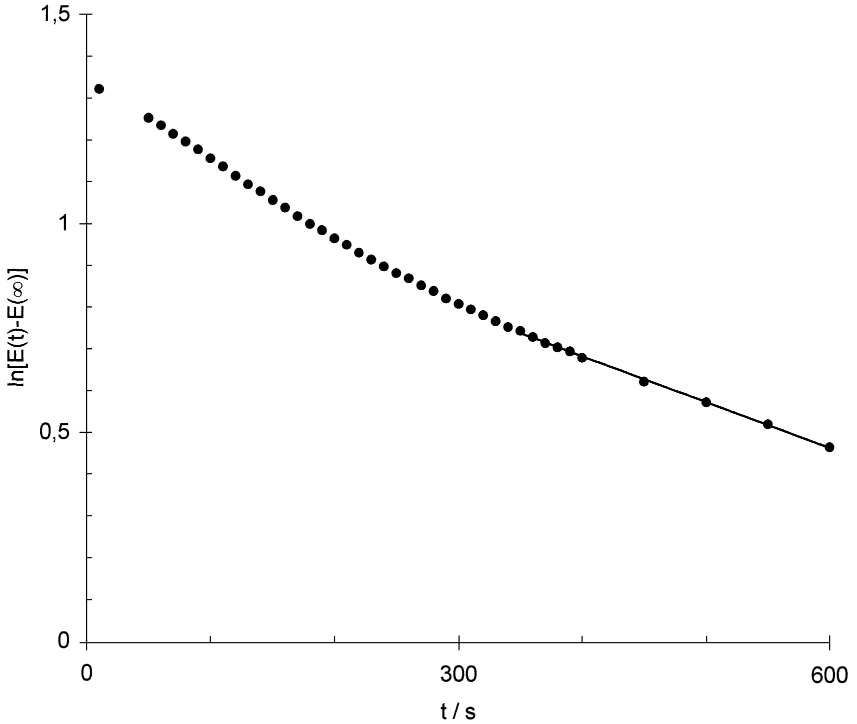

Fig. 2. Determination of the chemical diffusion coefficient at 640°C in $Pr_{0\cdot7}Ce_{0\cdot3}O_{2-x}$ ($x = 0\cdot667$) from the long-time approximation [eqn (3)].

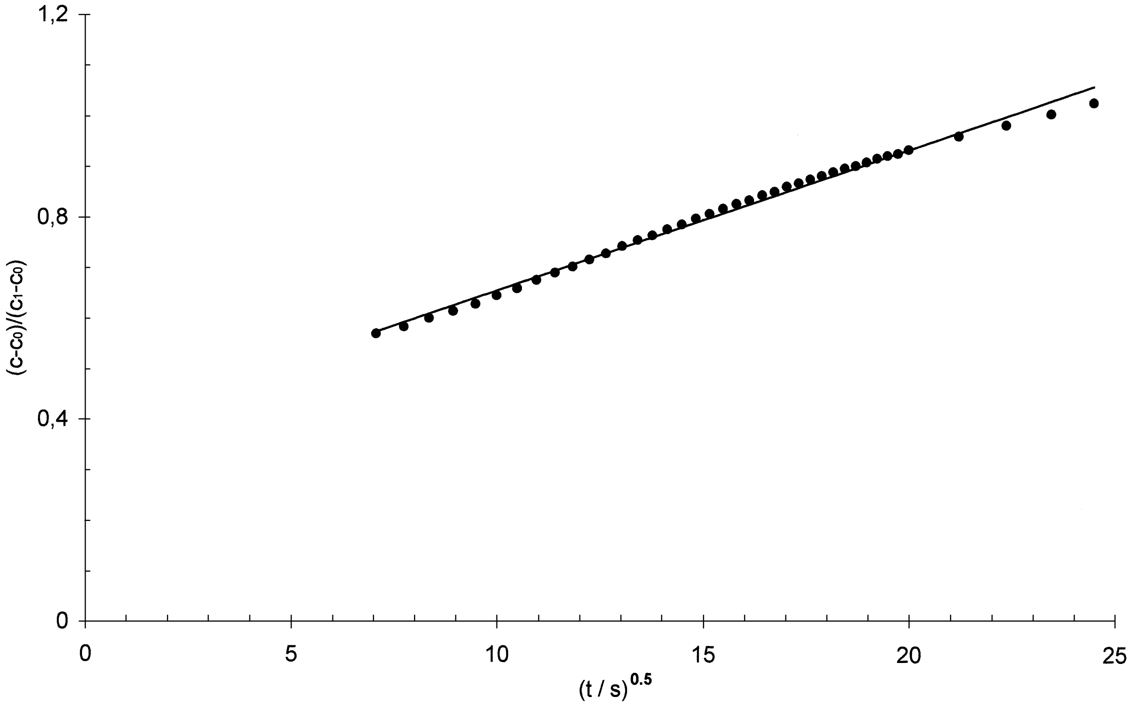

Fig. 3. Determination of the chemical diffusion coefficient at 640°C in $Pr_{0\cdot7}Ce_{0\cdot3}O_{2-x}$ ($x = 0\cdot667$) from the short-time approximation [eqn (4)].

establishment of equilibrium conditions was sluggish at 470°C, we did not determine the diffusion coefficients at this temperature.

5 Discussion

The oxygen pressure dependence at 560 and 640°C, with an exponent of $-1/6$, is in agreement with doubly charged oxygen vacancies as majority point defects. The power law dependence, based on an ideal mass action law,[10] applies in spite of the apparently high defect concentrations (Fig. 1). However, we are operating in the vicinity of an intermediate compound, in which the predominant part of the oxygen vacancies are structurally ordered and may not be considered as defects.

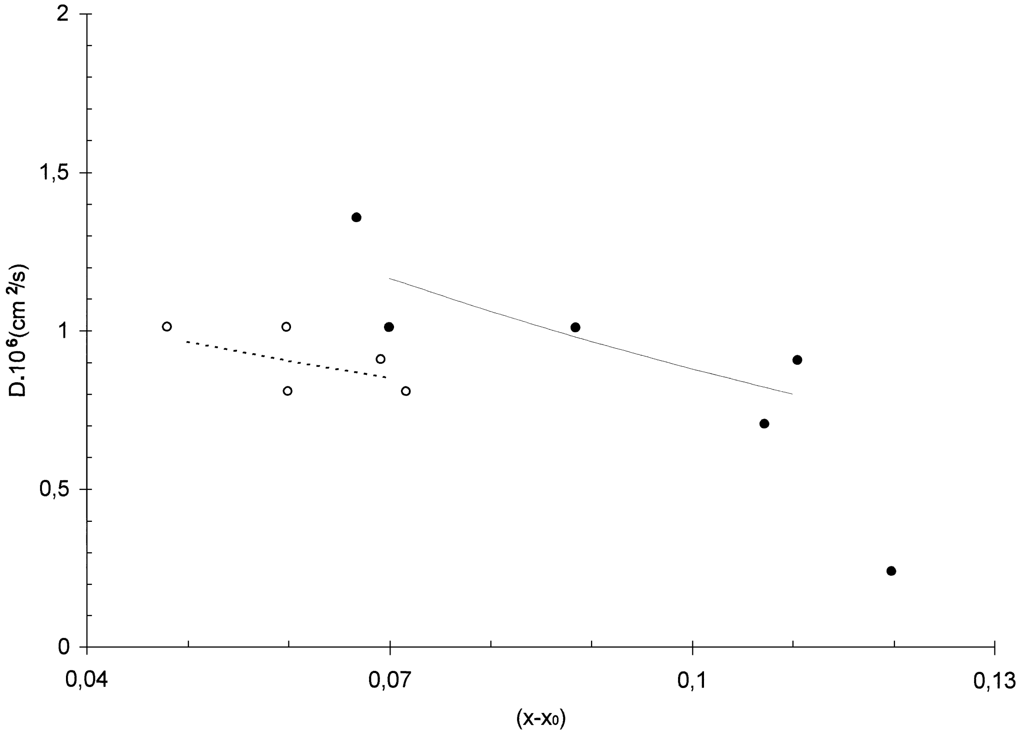

Fig. 4. Dependence of the chemical diffusion coefficient on the oxygen deficiency $(x-x_0)$ (●: 640°C, ○: 560°C).

Moreover, these systems exhibit rather high dielectric constants, which thereby significantly reduce Debye–Hückel type defect interactions. Consequently, ideal mass action laws appear to remain applicable.

Nevertheless, association phenomena between defects are possible at reduced temperatures. They can be taken into account by replacing mole fractions by activities or by considering new defect species. The formation of singly charged and uncharged oxygen vacancies can be considered as an association between doubly charged vacancies and electrons.[10] A similar derivation shows that the exponent for the oxygen pressure dependence should equal $-1/4$ or $-1/2$ for singly charged and uncharged vacancies, respectively. Experimentally, an exponent of $-1/3$ was found at 470°C, which may reflect the tendency for defect association between oxygen vacancies and electrons at low temperature. On the other hand, it cannot be excluded that equilibrium was not established at 470°C, the lowest temperature of measurement. Therefore, the agreement may be fortuitous.

The temperature dependence of the equilibrium constant gives a reduction enthalpy $\Delta H = (2{\cdot}9 \pm 0{\cdot}3)$ eV (280 kJ mol^{-1}). This value is lower than the corresponding value for conventional polycrystalline cerium dioxide (4·7 eV[16]), but higher than that for nanocrystalline cerium dioxide (2·3 eV[17]). While one may argue that this lower value is a consequence of the large number of interfacial sites in the nanocrystalline mixed oxide, where defect formation energies are reduced, e.g. nanocrystalline cerium oxide[17] and titanium dioxide,[18] it is more likely related to the lower reduction enthalpy of praseodymium oxide as compared to cerium oxide.

Concerning the kinetics of oxygen equilibration, the calculated chemical diffusion coefficients of the order of 10^{-6} cm^2 s^{-1} can be compared with mixed conducting binary oxides like PbO (D (500°C) $\approx 2\times10^{-7}$ cm^2 s^{-1})[11] and CeO_{2-x} (D (971°C) $\approx 6\times10^{-5}$ cm^{2}s^{-1})[19] or ternary oxides like $BaTiO_3$ (D (600°C) $\approx 10^{-8}$ cm^2/s^{-1}).[12]

An apparent activation energy of 0·3 eV (30 kJ mol^{-1}) was deduced from the two temperatures at which the diffusivity was determined. This value is low compared with activation energies for oxygen bulk diffusion commonly reported in fluorite oxides, e.g. 0·6 to 1·0 eV in CeO_2 and stabilized ZrO_2.[20] It is worth while examining the possible source of this low activation energy. First, enhanced intergranular diffusion is possible in a nanocrystalline oxide, given the high density of grain boundaries. The activation energy for intergranular diffusion is commonly smaller than that for bulk diffusion; an average reduction by 50% has been found in metallic systems.[14] Secondly, this being a mixed conductor, it is possible that under certain circumstances the electronic diffusivity is limiting which, at least in the CeO_2 end member, exhibits an activation energy of the order of 0·3–0·4 eV.[21]

6 Conclusion

The mixed oxide $Pr_{0\cdot7}Ce_{0\cdot3}O_{2-x}$ of approximate grain size of 35 nm exhibits a single phase region at intermediate $P(O_2)$ and an apparent two phase region at high $P(O_2)$. The level of non-stoichiometry, x, follows an approximate $P(O_2)^{-1/6}$ dependence in the single phase regime consistent with doubly ionized oxygen vacancies and electrons as the predominant defects, being formed with a reduction enthalpy of $\Delta H = (2\cdot9 \pm 0\cdot3)$ eV. The redox kinetics are characterized by chemical diffusivities of the order of $10^{-6}\,cm^2\,s^{-1}$ at 640°C and an activation energy of 0·3 eV. Nanocrystalline mixed praseodymium-cerium oxides are thus potentially useful oxygen storage materials given their enhanced oxygen deficiency and high rates of oxygen exchange and diffusion at temperatures in the range 550–650°C. The experimental results appear to be consistent with expected changes in defect formation and migration energies at interface sites, but more data on these and other systems are necessary to confirm such conclusions.

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