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Chemical relaxation experiments on mixed conducting oxides with large stoichiometry deviations

Andreas Falkenstein [a,c], David N. Mueller [a,b,c,*], Roger A. De Souza [a,c], Manfred Martin [a,c]

[a] Institute of Physical Chemistry, RWTH Aachen University, D-52056 Aachen, Germany
[b] Peter Gruenberg Institute (PGI-6), Research Centre Juelich, D-52425 Juelich, Germany
[c] JARA-Energy, Germany

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ABSTRACT

Relaxation techniques are widely used to determine the mass transport parameters of oxygen, namely the chemical surface exchange coefficient k_{chem} and the chemical diffusion coefficient D_{chem}, of mixed ionic-electronic conductors. The investigation of technologically relevant mixed conducting oxides that exhibit high values of both k_{chem} and D_{chem} by relaxation methods faces the problem that the amount of oxygen released or taken up by the sample during a relaxation experiment is not negligible. In fact, it can be of the same order as the amount supplied by the gas stream; the desired step-like change in oxygen activity that initiates the relaxation process thus becomes ill defined. In this study we examine strategies to identify and counteract this problem: As a model system we use the mixed ionic electronic conducting perovskite-type oxide $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, which exhibits extraordinarily high oxygen exchange kinetics, and we perform conductivity relaxation experiments that monitor the oxygen partial pressure in the vicinity of the sample.

1. Introduction

Chemical relaxation experiments constitute a well-established and widely used method for determining the chemical diffusion coefficient D_{chem} and the chemical surface exchange coefficient k_{chem} of oxygen in mixed ionic and electronic conducting oxides. The experiment consists, in principle, of instantaneously effecting a difference between the oxygen activity in an oxide sample and that in the surrounding gas phase. The change in a characteristic sample property, i.e. one that depends on the oxygen content of the sample, such as weight [1], conductivity [2,3], or colour [4–6], is then monitored as a function of time.

In practice, a truly instantaneous, i.e. step-like, change in oxygen activity is hard to achieve experimentally. For example, if the change in oxygen activity is effected by changing the oxygen partial pressure in the gas flowing through an experimental cell, the time constant for this change (the flush time), τ_Δ, can be of the order of seconds to minutes depending on the volume of the reactor and the gas flow rate. In order to obtain accurate values of D_{chem} and k_{chem} from a relaxation experiment, one should ensure that τ_Δ is orders of magnitude smaller than the measured relaxation time of the sample, τ_σ. As τ_Δ approaches τ_σ, it is still possible to correct for τ_Δ up to $10\tau_\Delta < \tau_\sigma$ [7]. If, however, the relaxation time is in the same range or even lower than the flush time, $\tau_\Delta \geq \tau_\sigma$, the sample acts effectively as an oxygen sensor. Thus, $\tau_\Delta \ll \tau_\sigma$ represents the first constraint of a chemical relaxation experiment.

A second constraint is that the magnitude of the change in oxygen activity should be large enough to yield a significant change in the relevant sample property as a function of time, but should not be so large that the response is no longer within the linear regime. The limits of the linear regime are likely to be different for D_{chem} [8] and k_{chem} [9].

In this study we examine a third constraint: The amount of oxygen leaving the sample per unit time, $\dot{n}_{sample}$, should be negligible compared to the amount of oxygen flowing past the sample in the same time, $\dot{n}_{gas}$, or in terms of fluxes and corresponding areas

$$j_{gas} \cdot A_{cell} \gg j_{in/out} \cdot A_{sample}, \tag{1}$$

where j_{gas} is the flux of oxygen in the gas phase; A_{cell} is the cross-sectional area of the cell; $j_{in/out}$ is the flux of oxygen released by or incorporated into the sample; and A_{sample} is the surface area of the sample. This constraint is especially important for materials that exhibit (i) high values of D_{chem} and k_{chem} and (ii) large changes in oxygen nonstoichiometry, $\Delta\delta$, even for small changes in oxygen partial pressure, ΔpO_2. Such conditions are met for the highly nonstoichiometric perovskite-oxide $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF5582) [10–12].

The problem of limited mass transport in the gas phase [i.e. when Eq. (1) is not satisfied] was first identified by Preis et al. [13] As a solution to this problem they suggested continuous modification of the pO_2 supplied to the sample so that the partial pressure of oxygen measured downstream of the sample remains constant. This solution leads,

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* Corresponding author at: Forschungszentrum Juelich GmbH, PGI-6, Leo-Brandt-Strasse, 52425 Juelich, Germany. Tel.: +49 2461 615814.
E-mail address: dav.mueller@fz-juelich.de (D.N. Mueller).

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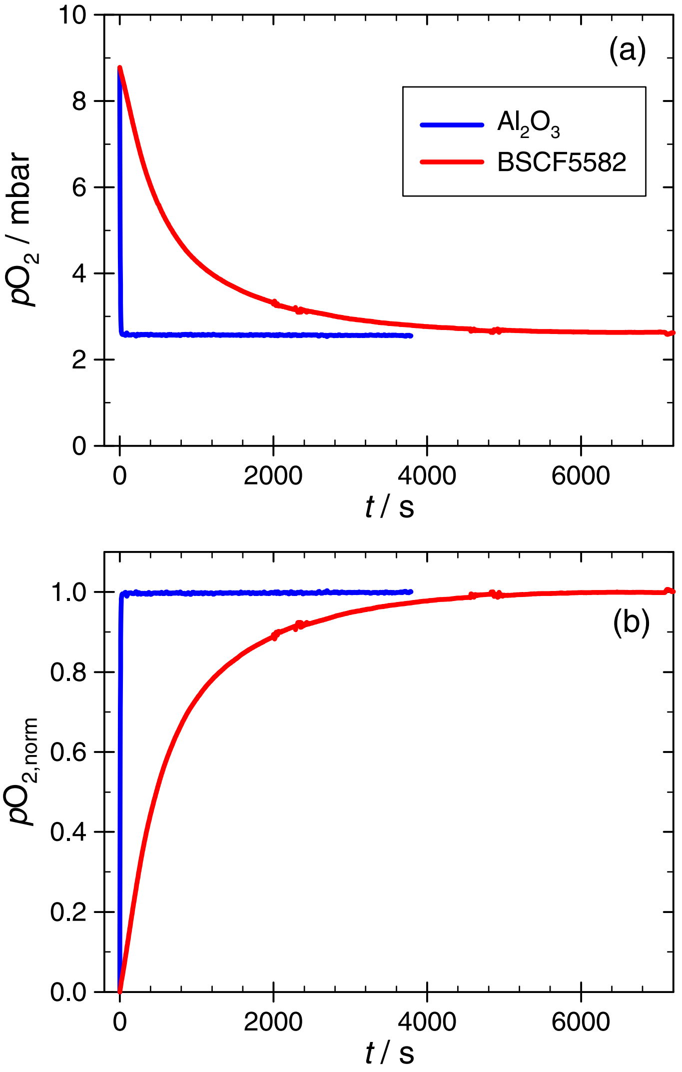

Fig. 1. (a) Response of a potentiometric oxygen sensor situated behind a sample (BSCF5582 sample or an inactive Al_2O_3 ingot of identical dimensions). $\Delta pO_2 = -6.2$ mbar (8.8 mbar → 2.6 mbar), $T = 1173$ K, $\dot{V} = 25$ mL min^{-1}, sample dimensions (rectangular slab): $2a = 4.2$ mm, $2b = 4.0$ mm, $2c = 33.0$ mm. (b) Normalisation of the data shown in (a).

however, to a variation as a function of time of the oxygen partial pressure to which the sample is exposed. Recently, Lohne et al. [14] examined the problem of limited gas-phase transport by finite element simulations. They showed that large errors are introduced into the obtained (effective) values of D_{chem} and k_{chem}. In this study we present, first, a method to identify when Eq. (1) is not fulfilled, and hence, when large errors are to be expected for the kinetic parameters obtained in a relaxation experiment. Second, we discuss strategies to optimise the experimental parameters to minimise such errors.

2. The problem

In Fig. 1 we compare the experimentally measured response of an oxygen sensor situated behind a sample (either "inactive" Al_2O_3 or "active" BSCF5582) exposed to the same step in pO_2. In the case of the inactive Al_2O_3 sample, the sensor response indicates the flush time of the reactor. For the conditions chosen in the experiment shown, $\tau_\Delta \approx 5$ s; where τ_Δ is given by modelling the reactor as a continuously stirred tank [15], $pO_{2,norm} = [pO_2(t) - pO_2(0)]/[pO_2(\infty) - pO_2(0)] = 1 - \exp(-t/\tau_\Delta)$. In comparison, the apparent flush time in the case of the BSCF5582 sample is orders of magnitude larger ($\tau_\Delta = 800$ s): this unambiguously indicates that BSCF5582 is releasing significantly large amounts of oxygen into the gas phase during the relaxation because τ_Δ should be independent of the type of sample present.

To circumvent this problem, it is evident from Eq. (1) that one must either increase the quantities on the left hand side or decrease those on the right hand side. Below we discuss four strategies.

To increase the left hand side, one can:

i Increase the gas flow rate $\dot{V}$ and thus increase the flux of oxygen, j_{gas}, whilst maintaining the same pO_2 in the carrier gas stream.
ii Increase the experimental cell volume (specifically the cross-sectional area A_{cell}), whilst maintaining the same flux, j_{gas}, by increasing the volume flux through the reactor, $\dot{V}$.

To decrease the right hand side, one can:

iii Reduce the amount of oxygen released/taken up by the sample by lowering the sample's volume. This lowers $j_{in/out}$ and A_{sample}.
iv Use smaller pO_2 steps in order to decrease the overall amount of oxygen released or taken up by the sample. This lowers $j_{in/out}$.

In the following we discuss each of these approaches, focussing mainly on the first of them. In this work, we consider relaxation experiments that monitor the electrical conductivity [2] (its principle is described in the appendix), although the conclusions we reach are universally applicable for all relaxation experiments.

3. Experimental

The apparatus used for conductivity relaxation measurements is schematically shown in Fig. 2. Two sets of mass flow controllers (MKS Instruments, Germany) are used to create two mixtures of oxygen and nitrogen (both 5.0 purity, Westfalen AG, Germany) of different pO_2. A

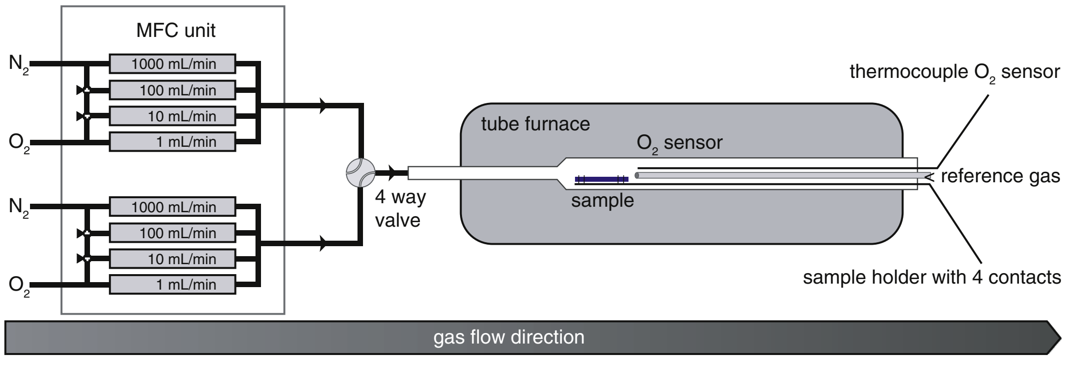

Fig. 2. Construction scheme of the relaxation apparatus.