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Reactor Flush Time Correction in Relaxation Experiments

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The present paper deals with the analysis of experimental data from conductivity relaxation experiments. It is shown that evaluation of the chemical diffusion and surface transfer coefficients for oxygen by use of this technique is possible only if accurate data for the conductivity transient can be measured at short times, *i.e.*, immediately after the step change in the surrounding oxygen partial pressure. The flushing behavior of the reactor volume may, however, significantly influence the early stage of the relaxation process. Large errors in the transport parameters are obtained from fitting the relaxation data to the theoretical equations if this phenomenon is not properly recognized. Equations are presented which describe the transient conductivity taking into account the finite flush time of the reactor. The regimes of surface- and diffusion-controlled kinetics are discussed quantitatively.
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Relaxation techniques offer a useful tool for obtaining the chemical diffusion and surface transfer coefficients for oxygen of mixed ionic electronic conductors. These materials are considered for application as electrodes in oxygen partial pressure sensors,[1] solid oxide fuel cells,[2] and as semipermeable membranes for the separation of oxygen from air[3] at high temperatures. The relaxation process follows after an instantaneous change of the oxygen activity in the gas phase and brings about a change in stoichiometry of the oxide. This change can be measured by monitoring the weight or electrical conductivity as a function of time. The oxygen transport parameters are obtained from fitting the experimental relaxation data to the theoretical equations, depending on the particular type of sample geometry. Examples of relaxation techniques include conductivity relaxation,[4-6] dynamic thermogravimetry,[7] and solid-state electrochemical methods.[8]

In general, the oxygen partial pressure in relaxation experiments is changed by switching between two gas flows with different oxygen partial pressures. In the derivation of the theoretical equations it is assumed that the oxygen partial pressure in the reactor is changed instantaneously. This assumption simplifies the mathematical treatment considerably. However, a correction must be applied if the relaxation time approaches the flush time of the reactor volume. In conductivity relaxation experiments, in which general reactor volumes are small and, hence, flush times are short, a flush-time correction is needed only if relaxation times are comparatively short, *e.g.*, at high temperatures. On the other hand, the flush times encountered in, for example, dynamic thermogravimetric experiments are usually large due to the inherently large reactor volumes. In these cases experimental limitations due to the finite flush time of the reactor are likely to occur at any temperature of interest. Erroneous results may be deduced from the experimental data if this phenomenon is not properly recognized.

In the present paper, equations are derived which describe the transient response in conductivity relaxation experiments, taking into account the time needed for reactor flushing. From the analysis of these equations, a number of experimental conditions are formulated, which should be met in relaxation-type experiments.

Ideal Step Response

In conductivity relaxation experiments the relation between stoichiometry and electrical conductivity is exploited. The time variation of the conductivity of the sample is measured in response to a different oxygen activity in the gas phase. The conductivity relaxes towards a new value as the oxide attains its new equilibrium state. The relaxation process is assumed to be controlled by chemical diffusion of oxygen and the associated surface transfer rate. There are many useful solutions to Fick's second law, depending upon the particular initial and boundary conditions. In this section, the change in the surrounding oxygen activity is taken to be instantaneous. The sample is considered to be a thin sheet, so that one-dimensional diffusion occurs. In the section on Nonideal step response, equations are presented to modify the general solution for this geometry and to incorporate the effect of a finite flush time of the reactor.

General solution.—One-dimensional diffusion of oxygen into a dense ceramic oxide can be described by Fick's first law

$$J = -\tilde{D}\frac{\partial c}{\partial x} \qquad [1]$$

in which J, $\tilde{D}$, and c are the particle flux density, the chemical diffusion coefficient, and the concentration of oxygen, respectively. Application of the continuity equation for the particle flux density leads to Fick's second law

$$\frac{\partial c}{\partial t} = \tilde{D}\frac{\partial^2 c}{\partial x^2} \qquad [2]$$

where it is assumed that the chemical diffusion coefficient $\tilde{D}$ is independent of concentration. The conditions for the flux density at both boundaries of the sample at $x = \pm a$ can be written as

$$J(a) = -\tilde{D}\frac{\partial c}{\partial x}\bigg|_{x=a} = K_{tr}[c(a) - c_\infty]$$

and

$$J(-a) = -\tilde{D}\frac{\partial c}{\partial x}\bigg|_{x=-a} = -K_{tr}[c(-a) - c_\infty] \qquad [3]$$

where K_{tr} is the surface transfer coefficient, $2a$ the sample thickness, and c_∞ the equilibrium concentration at infinite time after the step change in p_{O_2}. The solution for the concentration profile as a function of time, $c_{step}(x,t)$, is obtained through an eigenfunction expansion of the initial oxygen concentration[9] $c(x,0) = c_0$

$$\overline{c}_{step}(x,t) = \frac{c_{step}(x,t) - c_0}{c_\infty - c_0} = 1 - \sum_{n=1}^{\infty} \frac{2L_\alpha \cos(\alpha_n x/a)}{(\alpha_n^2 + L_\alpha^2 + L_\alpha)\cos(\alpha_n)} \exp\left(-\frac{t}{\tau_n}\right) \qquad [4]$$

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where the horizontal bar indicates that the quantity is made dimensionless. The time constants τ_n are given by

$$\tau_n = \frac{a^2}{\tilde{D} \cdot \alpha_n^2} \quad [5]$$

The time constants play an important role in the sense that the duration of the transient experiment is given by approximately four to five times the first time constant τ_1. After this period, the $n = 1$ term fades to almost zero as the oxide attains its new equilibrium state. Similarly, the $n = 2$ term fades after approximately four to five times the second time constant τ_2. As is discussed later, τ_2 (being much smaller than τ_1) can be determined only from the experimental relaxation data immediately after the step change in oxygen partial pressure. Values of both time constants are needed for proper evaluation of the chemical diffusion coefficient and the surface transfer rate simultaneously.

In Eq. 4, the parameter L_α and the eigenvalues α_n are solved from

$$\alpha_n \tan\alpha_n = \frac{aK_{tr}}{\tilde{D}} = L_\alpha \quad [6]$$

A simple method for numerical evaluation of the eigenvalues α_n was presented in Ref. 10. From this equation, a characteristic length scale L_c can be defined, given by

$$L_c = \frac{\tilde{D}}{K_{tr}} \quad [7]$$

As discussed in the next section, diffusion limitation occurs if $a \gg L_c$ and surface limitation if $a \ll L_c$.

Assuming a linear proportionality between the changes of the electronic conductivity and the oxygen concentration, the dimensionless transient conductivity $\overline{\sigma}_{step}(t)$ can be derived by integration of the concentration over the sample volume

$$\overline{\sigma}_{step}(t) = \frac{\sigma_{step}(t) - \sigma_0}{\sigma_\infty - \sigma_0} = 1 - \sum_{n=1}^{\infty} A_n \exp\left(-\frac{t}{\tau_n}\right) \quad [8]$$

where

$$A_n = \frac{2L_\alpha^2}{\alpha_n^2(\alpha_n^2 + L_\alpha^2 + L_\alpha)} \quad [9]$$

It is appropriate to mention here that the change of the conductivity may not be proportional to the change of the oxygen concentration. In addition, the linear rate law adopted for the surface reaction lacks a physical basis, which restricts the applicability of Eq. 3 in practice to small step changes in the ambient oxygen partial pressure. Obviously, the rate of the surface reaction will depend on the atmosphere used to control the oxygen partial pressure. The surface reaction rates will therefore be different in CO-CO_2 or H_2-H_2O mixtures.

Distinguishing between surface reaction and diffusion control.—Relaxation experiments are carried out for evaluation of the chemical diffusion coefficient $\tilde{D}$ and the surface transfer rate K_{tr}. In the most desirable case, the transient depends heavily on both parameters. Such a strong dependence guarantees accurate determination of both transport parameters from a single experiment. However, the relaxation may be dominated by only one of the transport processes. This is the case if the relaxation kinetics is under pure control of either the surface transfer reaction or the diffusion of the mobile species within the solid, as opposed to the situation where the kinetics is under mixed control.

In relaxation studies, $(\tilde{D}, K_{tr}, a)$ is usually taken as the independent set of parameters with which the transient response can be fully described. Instead, one might also consider (τ_1, τ_2, a). It can be shown that the transient is fully determined by this set.[a] The advantage is that clear criteria can be formulated to distinguish between surface- and diffusion-controlled kinetics. The first two time constants τ_1 and τ_2 have the highest values and, therefore, they can be evaluated with the highest precision. Higher terms in the series of Eq. 8 fade away faster, but they still contribute to the very early stage of the transient. These higher terms cannot be ignored, in spite of the focus on τ_1 and τ_2 in this work.

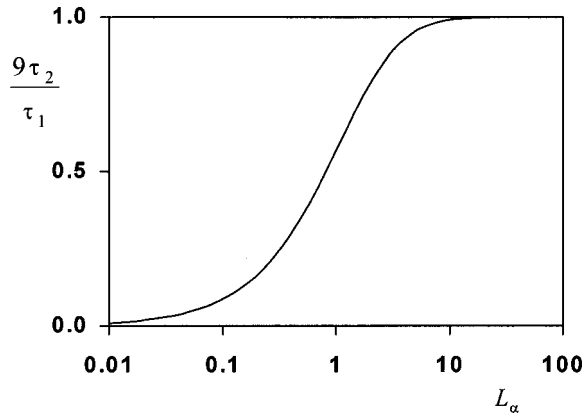

Figure 1. Ratio of τ_2 and τ_1 *vs.* L_α.

From the general solution presented by Eq. 8 constrained versions can be derived if the relaxation kinetics is under pure control by a limiting rate of the surface reaction or by that of the diffusion within the solid. If the relaxation is rate limited by the surface reaction, the time constants τ_n reduce to zero for $n \geq 2$. This can be expressed as

$$(\tau_1, \tau_2, a) = \left(\frac{a}{K_{tr}}, 0, a\right) \quad [10]$$

In the case of diffusion limitation within the solid the corresponding condition reads

$$(\tau_1, \tau_2, a) = \left(\frac{4a^2}{\pi^2\tilde{D}}, \frac{1}{9}\tau_1 = \frac{4a^2}{9\pi^2\tilde{D}}, a\right) \quad [11]$$

In this special case the values for the other time constants are given by $\tau_3 = (1/25)\tau_1$, $\tau_4 = (1/49)\tau_1$, $\tau_5 = (1/81)\tau_1$, ...

From the above it is apparent that the ratio τ_2/τ_1 is of relevance in the fitting procedure. In Fig. 1, this ratio is plotted as a function of L_α, which is a dimensionless transport number. For L_α values smaller than approximately 0.03, τ_2/τ_1 equals almost zero. The fit of the experimental data falling in this regime will be independent of the value of $\tilde{D}$. This is the regime where surface-controlled kinetics occurs. For L_α values larger than approximately 30, the ratio τ_2/τ_1 becomes almost constant at 1/9. Here, the fit of the relaxation data is independent of the value of K_{tr} due to diffusion-controlled kinetics. At intermediate values of L_α the relaxation process is under mixed control of surface transfer and diffusion. Only when the experimental data fall into this regime, accurate values for both $\tilde{D}$ and K_{tr} can be obtained from the fitting procedure. Since the latter regime covers the range from surface- to diffusion-controlled kinetics, restrict-

[a] From the ratio τ_2/τ_1, the value of L_α can be obtained as suggested by Fig. 1. Subsequently, the eigenvalue α_1 can be solved using Eq. 6. The full set follows from $(\tilde{D}, K_{tr}, a) = (a^2/\tau_1\alpha_1^2, aL/\tau_1\alpha_1^2, a)$, using Eq. 5. This proves that the set $(\tilde{D}, K_{tr}, a)$ can be obtained from the set (τ_1, τ_2, a).

ing L_α to values between 0.03 and 30 in the fitting procedure allows for proper evaluation of τ_1 and τ_2, which are needed to evaluate both $\tilde{D}$ and K_{tr} simultaneously.

Critical L_α values distinguishing between diffusion, mixed- and surface-controlled regimes were suggested by Viani *et al.*,[11] however, the important relation between L_α and the ratio of τ_1 and τ_2 was not discussed by these authors.

Flush-Time Correction

Nonideal step response.—In this section a gradual equilibration of the oxygen partial pressure due to the finite time required for flushing the reactor volume is considered. The boundary conditions in this case read

$$J(a) = -\tilde{D}\frac{\partial c}{\partial x}\bigg|_{x=a} = K_{tr}[c(a) - c_{eq}]$$

and

$$J(-a) = -\tilde{D}\frac{\partial c}{\partial x}\bigg|_{x=-a} = -K_{tr}[c(-a) - c_{eq}] \quad [12]$$

where $c_{eq}(p_{O_2})$ denotes the equilibrium oxygen concentration which, in contrast to c_∞ in Eq. 3, is now a function of time.

The idealized step can be described using the Heaviside function $u(t)$. This function is defined to be zero for negative values of t and unity for positive values. The step change in oxygen partial pressure can thus be expressed as

$$p_{step}(t) = p_0 + (p_\infty - p_0) \cdot u(t) \quad [13]$$

or in a more convenient dimensionless form

$$\overline{p}_{step}(t) = \frac{p_{step}(t) - p_0}{p_\infty - p_0} = u(t) \quad [14]$$

Assuming continuously ideally stirred tank reactor (CISTR)[12] behavior in the actual reactor volume, the oxygen partial pressure as a function of time $p_{CISTR}(t)$ can be derived to be

$$p_{CISTR}(t) = p_\infty + (p_0 - p_\infty) \cdot \exp\left(-\frac{t}{\tau_f}\right) \quad [15]$$

with

$$\tau_f = \frac{V_r}{\Phi_{v,tot}} \cdot \frac{T_{STP}}{T_r} \quad [16]$$

where $\Phi_{v,tot}$ is the flow rate of gas. V_r and T_r denote the reactor volume and temperature, respectively, while T_{STP} refers to room temperature. The dimensionless oxygen partial pressure can be written as

$$\overline{p}_{CISTR}(t) = \frac{p_{CISTR}(t) - p_\infty}{p_0 - p_\infty} = \exp\left(-\frac{t}{\tau_f}\right) \quad [17]$$

In the derivation it is assumed that the oxygen release and uptake by the sample is negligible. The time constant τ_f, referred to as the flush time in this paper, denotes the characteristic time needed to flush the reactor volume. From Eq. 17 it is calculated that after a period of $4 \times \tau_f$ has elapsed, only 1.83% of the original reactor gas volume has not been replaced yet. It should be noted that the validity of Eq. 17 extends not only to N_2-O_2 mixtures, but also to CO-CO_2 and H_2-H_2O mixtures, since it can safely be assumed that gas-phase reactions do not occur.

The transient conductivity can be calculated in several ways. Inspired by digital signal analysis,[13] Eq. 17 can be written as the sum of an infinite number of impulses. The response of the conductivity to each impulse (Dirac δ-peak) of the oxygen partial pressure can be evaluated. By applying the superposition theorem, the flush-time-corrected conductivity transient is given by the superposition of the impulse responses. This is similar to the method presented below, which uses the convolution theorem in the Laplace domain; the Laplace transform method is applied here because it is more transparent.

In the derivation a dimensionless transfer function $\overline{H}(s)$ is used, defined as

$$\overline{H}(s) = \frac{\mathbf{L}[\overline{\sigma}_{step}(t)]}{\mathbf{L}[\overline{p}_{step}(t)]} \quad [18]$$

in which **L** denotes the Laplace transform operator, given by

$$\mathbf{L}[f(t)] := \int_0^\infty f(t) \cdot \exp(-st)dt \quad [19]$$

Using this definition, $\overline{H}(s)$ can be expressed in the form

$$\overline{H}(s) = \frac{\mathbf{L}[\overline{\sigma}_{step}(t)]}{\mathbf{L}[\overline{p}_{step}(t)]} = s \cdot \left[\frac{1}{s} - \sum_{n=1}^{\infty} \frac{A_n \cdot \tau_n}{1 + s \cdot \tau_n}\right] \quad [20]$$

The Laplace transform $\mathbf{L}[\overline{p}_{CISTR}(t)]$ can be obtained similarly

$$\mathbf{L}[\overline{p}_{CISTR}(t)] = \frac{\tau_f}{1 + s \cdot \tau_f} \quad [21]$$

The Laplace transform $\mathbf{L}[\overline{\sigma}_{CISTR}(t)]$ is given by[b]

$$\mathbf{L}[\overline{\sigma}_{CISTR}(t)] = -\overline{H}(s) \cdot \mathbf{L}[\overline{p}_{CISTR}(t)] = -\frac{s\tau_f}{1 + s\tau_f} \cdot \left[\frac{1}{s} - \sum_{n=1}^{\infty} \frac{A_n \cdot \tau_n}{1 + s \cdot \tau_n}\right] \quad [22]$$

The conductivity transient in the time domain is obtained by the inverse Laplace transform of Eq. 22. The convolution theorem[14] states that the product of the Laplace transforms of two functions $f(t)$ and $g(t)$ equals

$$\mathbf{L}(f*g) = \mathbf{L}(f) \cdot \mathbf{L}(g) = \mathbf{L}\left[\int_0^t f(\tau) \cdot g(t - \tau)d\tau\right] \quad [23]$$

This theorem can be used to obtain the response to the CISTR behavior of the reactor if two functions can be found such that the product of their Laplace transforms equals the right side of Eq. 22. Two functions satisfying this condition are

$$f(t) = -\frac{1}{\tau_f} \cdot \exp\left(-\frac{t}{\tau_f}\right) \text{ and } g(t) = 1 - \sum_{n=1}^{\infty} A_n \cdot \exp\left(-\frac{t}{\tau_n}\right) \quad [24]$$

This leaves the integral

$$\overline{\sigma}_{CISTR}(t) = -\int_0^t \left[1 - \sum_{n=1}^{\infty} A_n \cdot \exp\left(-\frac{t}{\tau_n}\right)\right] \cdot \left[-\frac{1}{\tau_f}\exp\left(-\frac{t - \tau}{\tau_f}\right)\right] d\tau \quad [25]$$

to be evaluated. The final equation, which takes the flush time into account, is

[b] Note that a minus sign appears in this equation, because both pressure transients were not made dimensionless in the same way.

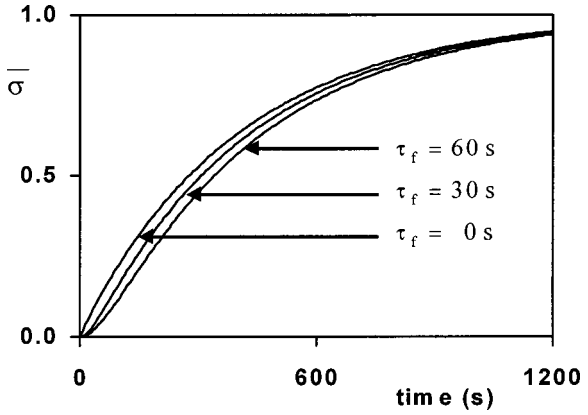

Figure 2. Three transients with different flush times.

$$\overline{\sigma}_{\mathrm{CISTR}}(t) = 1 - \exp\left(-\frac{t}{\tau_f}\right) - \sum_{n=1}^{\infty} A_n \cdot \frac{\tau_n}{\tau_n - \tau_f} \cdot \left[\exp\left(-\frac{t}{\tau_n}\right) - \exp\left(-\frac{t}{\tau_f}\right)\right] \quad [26]$$

Three different transients, calculated from Eq. 26, are presented in Fig. 2. The sample thickness is taken to be 0.04 cm. $\tilde{D}$ and K_{tr} are $1.6 \cdot 10^{-4}$ cm^2 s^{-1} and $6.3 \cdot 10^{-4}$cm s^{-1}, respectively. The transients are calculated for flush times of 0, 30, and 60 s. Note that the effect of the flush time is most pronounced in the early stage of the relaxation process. Whereas the ideal step response initiates immediately at $t = 0$, the effect of increasing the flush time is that it leads to a more gradual behavior in the early stage of the relaxation process.

Flush-time correction for other sample geometries.—Thus far, only the case of one-dimensional diffusion was considered. This case can be generalized to obtain the flush-time correction equations for many other sample geometries. For long cylindrical samples with radius R, only the equations for the pre-exponential factors A_n and the time constants τ_n need to be changed

$$A_n = \frac{4L_\rho^2}{\rho_n^2 \cdot (\rho_n^2 + L_\rho^2)} \quad [27]$$

and

$$\tau_n = \frac{R^2}{\rho_n^2 \tilde{D}} \quad [28]$$

The eigenvalues are now obtained from a different equation

$$\rho_n J_1(\rho_n) = L_\rho J_0(\rho_n) = \frac{RK_{tr}}{\tilde{D}} J_0(\rho_n) \quad [29]$$

in which J_0 and J_1 denote the first and second Bessel functions of the first kind, and R denotes the sample radius. The flush-time-corrected response is still given by Eq. 26 as before.

Other diffusion problems can be treated similarly. For long beams and short cylinders, the general form of the equation without flush-time correction reads

$$\overline{\sigma}_{\mathrm{step}}(t) = 1 - \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} A_{n,m} \cdot \exp\left(-\frac{t}{\tau_{n,m}}\right) \quad [30]$$

By analogy with Eq. 26, the general form of the response with flush-time correction can be deduced to be

$$\overline{\sigma}_{\mathrm{CISTR}}(t) = 1 - \exp\left(-\frac{t}{\tau_f}\right) - \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} A_{n,m} \cdot \frac{\tau_{n,m}}{\tau_{n,m} - \tau_f} \cdot \left[\exp\left(-\frac{t}{\tau_{n,m}}\right) - \exp\left(-\frac{t}{\tau_f}\right)\right] \quad [31]$$

For two-dimensional diffusion in beam-shaped samples with a rectangular cross section $2a \times 2b$, the pre-exponential factors and time constants are given by

$$A_{n,m} = \frac{2L_\alpha^2}{\alpha_n^2(\alpha_n^2 + L_\alpha^2 + L_\alpha)} \cdot \frac{2L_\beta^2}{\beta_m^2(\beta_m^2 + L_\beta^2 + L_\beta)} \quad [32]$$

and

$$\tau_{n,m} = \frac{1}{\tilde{D} \cdot \left[\left(\frac{\alpha_n}{a}\right)^2 + \left(\frac{\beta_m}{b}\right)^2\right]} \quad [33]$$

In this equation, α_n denotes the roots of Eq. 6, while β_n denotes the roots of a similar equation

$$\beta_n \tan\beta_n = \frac{bK_{tr}}{\tilde{D}} = L_\beta \quad [34]$$

For three-dimensional diffusion in short cylinders[4] of radius R and length $2a$, the pre-exponential factors $A_{n,m}$ and time constants $\tau_{n,m}$ are given by

$$A_{n,m} = \frac{4L_\rho^2}{\rho_n^2 \cdot (\rho_n^2 + L_\rho^2)} \cdot \frac{2L_\alpha^2}{\alpha_n^2 \cdot (\alpha_n^2 + L_\alpha + L_\alpha^2)} \quad [35]$$

and

$$\tau_{n,m} = \frac{1}{\tilde{D}\left[\left(\frac{\alpha_n}{a}\right)^2 + \left(\frac{\rho_m}{R}\right)^2\right]} \quad [36]$$

where the eigenvalues α_n and ρ_n are given by Eq. 6 and 29, respectively.

Discussion

A number of conclusions can be drawn from Eq. 26. In the discussion given below, only the case of the thin sheet geometry is considered. However, the conclusions drawn remain valid for other sample geometries as well. Key parameters are the flush-time τ_f, the first and second time constants, τ_1 and τ_2. Different regimes can be distinguished depending on the ratio between these parameters. The regimes of interest are shown in Fig. 3 and are discussed separately in the following sections.

Fast flushing regime.—If reactor flushing is fast compared to the relaxation process, the final oxygen pressure of the ambient is quickly achieved and the conductivity response approaches the ideal step response, given by Eq. 8. This regime is referred to as ''Fast flushing regime'' in Fig. 3. From the mathematical point of view, the $\exp(-t/\tau_f)$ terms Eq. 26 can be neglected, while the first few $\tau_n/(\tau_n - \tau_f)$ terms approach unity. This regime is found for $\tau_2 \gtrsim 20\tau_f$.

A general rule of thumb for this regime follows from the following argument. The time needed for a single experiment is four to five times the first time constant τ_1. The second time constant τ_2 is nine times smaller than τ_1 in the case of diffusion limitation. In the

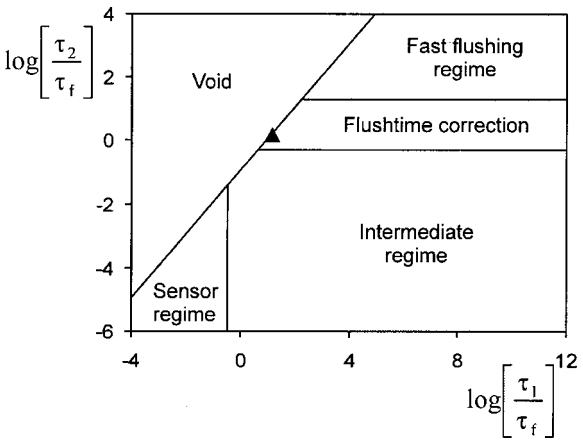

Figure 3. Depending on the values of the first two time constants, four regimes can be distinguished. The regime where the flush-time correction is needed is indicated. The triangular marker corresponds to the transient of Fig. 4 with a 20 s flush time.

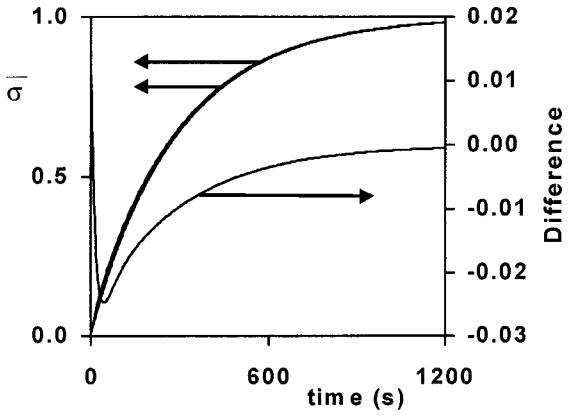

Figure 4. Two dimensionless transients. Although the difference is very small (right side axis), the transport parameters deduced from both curves differ significantly.

case of mixed control, τ_2 becomes even smaller, as discussed in the section Distinguishing between surface reaction and diffusion control. Proper evaluation of parameters from experimental data involves accurate determination of both τ_1 and τ_2. In order to be able to correctly neglect flushing behavior, the flush-time τ_f should be at least ten times smaller than τ_2. In conclusion, the flush time should be at least 500 times smaller than the duration of the experiment if diffusion limitation is assumed, and 5000 times smaller in the case where the regime of mixed control changes to pure surface limitation.

Slow reactor flushing; sensor regime.—In this regime the sample remains in quasi-thermodynamic equilibrium with the ambient during the flushing itself. Although the oxygen partial pressure is changed, the sample reacts fast so that the equilibrium between gas-phase oxygen and sample oxygen is maintained. Basically, the sample behaves as an oxygen sensor. This regime is therefore referred to as ''sensor regime'' in Fig. 3. No quantitative information on the transport parameters can be obtained from experimental data in this regime. It can only be applied to measure the flush time experimentally. The sensor regime occurs if the first time constant τ_1 is less than approximately one-third of the flush-time τ_f.

In conductivity relaxation experiments, the reactor volume is generally a few tens of milliliters, while the temperature ratio in Eq. 16 is of the order of three to four. With a flow rate of 100 mL min^{-1}, a flush time of the order of seconds is expected. However for thermogravimetric experiments, the reactor volumes tend to be much larger. These can be as large as 5 L, which results in a flush time of 13-17 min. Therefore, thermogravimetric analysis (TGA) experiments in which the dynamic response with respect to an oxygen partial pressure step is measured are virtually impossible.

Intermediate regime.—In this regime, τ_2 cannot be evaluated since $2\tau_2 \gtrapprox \tau_f$. It becomes impossible to obtain data on both $\tilde{D}$ and K_{tr} simultaneously. The only parameter that can be obtained from the fitting procedure is the value of K_{tr} provided that $L_\alpha < 0.03$ can be assumed, as discussed in the section on Distinguishing between surface reaction and diffusion control.

Flush-time correction regime.—In this regime, the flush time is of the same order of magnitude as τ_2. Equation 26 should be applied for evaluation of $\tilde{D}$ and K_{tr}. Neglecting flush-time effects can lead to large errors in these parameters. This can be illustrated using the simulated data presented in Fig. 4. Here, two transients are plotted for one-dimensional diffusion in a planar sample of 0.5 mm thickness. The difference between the transients is indicated also. One graph was simulated with a flush time of 20 s; $\tilde{D}$ and K_{tr} values were taken to be $1.47 \cdot 10^{-6}$ and $1.75 \cdot 10^{-4}$ cm s^{-1}, respectively. Using these values, τ_1 and τ_2 are calculated to be 300 and 29.4 s, respectively. The selected values correspond to the triangular marker in Fig. 3. The other transient was calculated neglecting the flush-time correction, using Eq. 8; $\tilde{D}$ and K_{tr} were taken to be $4.60 \cdot 10^{-6}$ and $1.00 \cdot 10^{-4}$ cm s^{-1}. The relaxation behavior is in the regime of mixed control ($L_\alpha = 2.98$), where it can be expected that both $\tilde{D}$ and K_{tr} can be evaluated accurately. The difference in the transients is very small. However, a discrepancy of more than a factor of three is observed for $\tilde{D}$. The error in the value of K_{tr} is as large as 75%. The flush time is much smaller than the duration of the experiment, but still large differences in $\tilde{D}$ and K_{tr} are found. This clearly indicates the importance of taking the flushing behavior of the reactor cell into account.

It may be difficult to detect which of the regimes in Fig. 3 prevails from an experiment. A hint in the direction of the sensor regime can be obtained from the temperature dependence of τ_1. Since both chemical diffusion and oxygen surface transfer are thermally activated processes, τ_1 should show significant temperature dependence. If the system is in the sensor regime, a curve fit without flush- time correction to a transient can still appear satisfactory. In this case, the time constant derived from the transient is misinterpreted as τ_1, rather than the flush-time τ_f. As indicated in Eq. 16, τ_f hardly depends on temperature. Therefore, an Arrhenius plot of the first time constant can reveal whether or not the system is in the sensor regime. If it is suspected that the system is in the sensor regime, a relaxation experiment can be performed in which the flushing gas flow rate is reduced by a factor of three. If the sensor regime holds, the sample responds three times slower, while only a minor change of the relaxation transient is observed if the sample is in the regime of surface limitation.

Measurement of Flush Times

In order to measure the flushing characteristics of the reactor volume, a new type of oxygen sensor was developed. The sensor does not yield an absolute value of the oxygen partial pressure, but it is extremely sensitive towards rapid changes in the oxygen partial pressure in the ambient. As can be deduced from Eq. 5, τ_1 decreases with decreasing sample thickness. Therefore, for sufficiently thin samples, the response time of the sample becomes much smaller than the time needed to flush the cell. This means that the sample behaves as a sensor for a change in the oxygen partial pressure, while its response can still be measured in an experiment like any other sample.

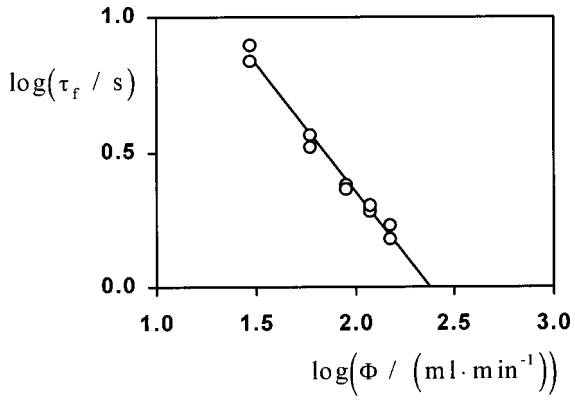

Figure 5. Reactor flush time *vs.* flow rate. The theoretically expected inverse proportionality between the flush time and the flow rate is indeed observed.

The sensor was made by depositing a porous 500 nm layer of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ on a 30% porous α-alumina disk by pulsed laser deposition.[15] Because gas-phase diffusion is extremely fast, the porosity of the substrate can be neglected; it is unimportant for the sensor's response time. A lock-in amplifier (EG&G Princeton Applied Research 5210) was used to measure the sensor response. The lock-in integration time was set to 100 ms. The short integration time was chosen because longer times would lead to misinterpretation of the sensor signal.

The experimental setup for conductivity relaxation is described in detail elsewhere.[5] The reactor has a total internal volume of approximately 28 cm^3. The total gas flow rate is set to 300 mL min^{-1}. From these data, the flush time of the reactor cell was estimated to be 1.4 to 1.9 s, using Eq. 16 for the flush time. The experimental data was fitted to

$$\overline{\sigma}_{\mathrm{CISTR}}(t) = 1 - \exp\left(- \frac{t}{\tau_f} \right) \qquad [37]$$

The flush time of the reactor volume depends strongly on the gas flow rate. The flush time was measured as a function of the total flow rate, switching the gas flow rates from 35.5% oxygen at 300 mL min^{-1} to 100% oxygen at various flow rates. The results are presented in Fig. 5. The reactor temperature was constant at 650°C. Good agreement with theory (Eq. 16 and 37) is observed, as indicated by the circular markers. A fit of the flush times shows that the response time is inversely proportional to the flow, as indicated by the straight line in the figure.

Conclusions

Depending on the values of the transport parameters, the transient is controlled by either diffusion, surface transfer kinetics, or both. For $L_\alpha = aK_{tr}/\tilde{D} < 0.03$, the surface transfer is rate limiting, while for $L_\alpha > 30$, diffusion is rate limiting. In the remaining case, a regime of mixed control exists. In curve fitting routines, limiting the value of L_α between 0.03 and 30 enables correct evaluation of both time constants τ_1 and τ_2. This is shown to be essential for accurate determination of both transport parameters $\tilde{D}$ and K_{tr}.

Four different regimes can be distinguished based on the values of the first and second time constants of the transient, and the characteristic time needed to flush the reactor volume. Both transport parameters $\tilde{D}$ and K_{tr} can be obtained under the conditions $0.03 < L_\alpha < 30$ and $\tau_f < 2\cdot\tau_2$. For $\tau_2 \gtrapprox 20\cdot\tau_f$, the transient equation associated with fast flushing can be applied. In the case where $\tau_1 \gg \tau_2, \tau_f$, only K_{tr} can be determined. It was demonstrated that a correction is necessary if the sample reacts fast with respect to the time needed to flush the reactor. Assuming that the reactor volume can be regarded as a continuously ideally stirred tank reactor, analytical equations for the relaxation transient were derived for several sample geometries.

A method to measure the flush time experimentally was presented. It is based on the fact that thin samples show fast relaxation behavior.

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