Oxygen exchange at gas/oxide interfaces: how the apparent activation energy of the surface exchange coefficient depends on the kinetic regime

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In the dedicated literature the oxygen surface exchange coefficient K_O and the equilibrium oxygen exchange rate $\mathfrak{R}_O^0$ are considered to be directly proportional to each other regardless of the experimental circumstances. Recent experimental observations, however, contradict the consequences of this assumption. Most surprising is the finding that the apparent activation energy of K_O depends dramatically on the kinetic regime in which it has been determined, *i.e.* surface exchange controlled *vs.* mixed or diffusion controlled. This work demonstrates how the diffusion boundary condition at the gas/solid interface inevitably entails a correlation between the oxygen surface exchange coefficient K_O and the oxygen self-diffusion coefficient D_O in the bulk ("on top" of the correlation between K_O and $\mathfrak{R}_O^0$ for the pure surface exchange regime). The model can thus quantitatively explain the range of apparent activation energies measured in the different regimes: in the surface exchange regime the apparent activation energy only contains the contribution of the equilibrium exchange rate, whereas in the mixed or in the diffusion controlled regime the contribution of the oxygen self-diffusivity has also to be taken into account, which may yield significantly higher apparent activation energies and simultaneously quantifies the correlation $K_O \propto D_O^{1/2}$ observed for a large number of oxides in the mixed or diffusion controlled regime, respectively.

As early as 1996 Kilner *et al.*[1] showed that there is, for a large number of different materials, a quite obvious correlation $K_O \propto D_O^{1/2}$ between the oxygen surface exchange coefficient K_O and the oxygen diffusion coefficient D_O (over almost 10 (!) orders of magnitude for D_O) for a number of perovskite compositions (with predominant electronic conductivity). Despite this empirical evidence it is assumed until to date,[2–4] however, that K_O and D_O are independent parameters, each of which reflects an independent microscopic mechanism. A major reason for this picture can be identified in the methodology of standard oxygen exchange experiments:[5] Here the oxygen

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flux j_O^K through a surface element subject to a concentration difference Δc_O is expressed as follows

$$j_O^K(0) = -K_O \Delta c_O(0) \tag{1}$$

The phenomenological eqn (1) defines K_O without recurring to any microscopic mechanism. As eqn (1) is only valid for surface reactions at $x = 0$ it seemed plausible that K_O depends exclusively on the defect chemistry of the surface. In 1998 Maier[6] proposed a relation between K_O and the equilibrium oxygen exchange rate $\mathfrak{R}_O^0$ at the gas/solid interface (s. Maier,[6] p. 222, eqn (149))

$$\frac{K_O}{\Delta x} = \frac{\mathfrak{R}_O^0}{c_O(0)} w_O(0) \quad \text{with} \quad w_O(0) \equiv \frac{c_O(0)}{RT} \frac{\partial \mu_O}{\partial c_O}\bigg|_{x=0} \tag{2}$$

where $c_O(0)$ is the oxygen equilibrium concentration near the surface, $w_O(0)$ is the thermodynamic factor near the surface, R and T have the usual meaning, and μ_O is the chemical potential of oxygen. $\mathfrak{R}_O^0$ is the oxygen exchange rate of the rate determining step in a consecutive reaction sequence.[7,8] Without violating Maier's universally valid original approach, in the literature[4,9–14] also an effective oxygen exchange rate $(1/\mathfrak{R}_O^0 = \sum_{i=1}^{n} 1/\mathfrak{R}_i$, n = number of consecutive reactions) is used to describe so-called consecutive "heterogeneous" reactions. The quantitative measure of the parameter Δx (with the dimension of a length) having been left undefined, Maier's suggestion essentially means that K_O is proportional to $\mathfrak{R}_O^0$.[15]

For the oxygen isotope exchange the thermodynamic factor is unity and eqn (2) yields $\tilde{K}_O = w(0)K_O^*$. (Throughout the text an asterisk characterizes a parameter determined in an isotope exchange experiment, whereas a tilde refers to a parameter determined in a chemical exchange experiment.) From $\tilde{D}_O = w(0)D_O = w(0)D_O^*/f_O$, where D_O is the self-diffusion coefficient and D_O^* is the tracer diffusion coefficient of oxygen, respectively, follows with the correlation factor $f_O \simeq 1$ a simple theoretical correlation.[15]

$$\frac{K_O^*}{D_O^*} \cong \frac{\tilde{K}_O}{\tilde{D}_O} \tag{3}$$

In 2006 De Souza[7] explicitly pointed out that there is a generally observed discrepancy between experimentally determined K_O/D_O ratios and the theoretically expected ratios according to eqn (3). Instead of fulfilling eqn (3) the experimental data yield $K_O^*/D_O^* > \tilde{K}_O/\tilde{D}_O$. This was a first significant experimental indication that eqn (2) might not fully take into account all aspects of the problem.

Armstrong *et al.*[12,13] used in 2011 and 2013 a novel experimental approach, called isothermal isotope exchange (IIE), to extract accurate K_O^* values in a surface exchange controlled regime. This technique relies on the exchange of isotopically labelled oxygen for lattice oxygen in a similar way to isotope exchange depth profiling (IEDP) with secondary ion mass spectrometry (SIMS), but is conducted *in situ* on powder samples (particle size 200–300 nm). In this way the exchange kinetics can be expected to be clearly in the surface exchange regime. Very unexpectedly Armstrong *et al.*[12,13] found apparent activation energies of K_O^* with negative (!) or very small positive values for different lanthanum based MIEC perovskite oxides like LC, LF, LSM, LSF, LSC or LSCF, but also for the standard oxygen ion conductors YSZ and GDC, which have fluorite structure. The reported range of apparent activation energies of the oxygen tracer surface exchange coefficient is −97 kJ mol^{-1} to +12 kJ mol^{-1} and is in strong contrast to the reported range from +60 kJ mol^{-1} to +333 kJ mol^{-1} measured by conventional methods generally using macroscopic sample geometries, *i.e.* IEDP/SIMS and electrical conductivity relaxation (ECR) (s. Armstrong *et al.*,[13] Table 5), but also measured by other powder-based methods like pulsed isotope exchange (PIE)[9–11] and long-term gas phase exchange/analysis GPE/GPA.[4,14,16] These experimental results suggest that the measured oxygen surface exchange coefficient K_O, if measured in the mixed regime and in the diffusion controlled regime, may depend not only on the equilibrium oxygen exchange rate $\Re_O^0$ at the gas/solid interface but also on the oxygen diffusion coefficient D_O in the bulk. Such a behaviour would clearly contradict eqn (2) which postulates that K_O depends on $\Re_O^0$ only in all kinetic regimes.

In 2015 Knoblauch *et al.*[17] performed thermogravimetric relaxation experiments on sintered CeO$_2$ pellets (1 mm thickness, 93% of theoretical density) with a grain size of about 20 μm. Because of the strongly enhanced chemical diffusivity[18] during the oxygen reduction step of nominally undoped CeO$_2$ Knoblauch *et al.*[17] concluded that their reduction experiments had been performed in the surface exchange regime. They also reported an apparent negative activation energy of −64 kJ mol^{-1} for $\tilde{K}_O$. That is, the work of Knoblauch *et al.*[17] showed that the apparent activation energy of the chemical oxygen surface exchange coefficient $\tilde{K}_O$ can also have negative values if it is measured in the surface exchange controlled regime.

The experimental contradictions to the general validity (*i.e.* in all kinetic regimes) of eqn (2) necessitate a rediscussion of the meaning of the parameter K_O. In order to facilitate a fundamental theoretical discussion the experimental situation of the oxygen exchange experiments is idealized as far as possible. In analogy to Maier[6] jump relaxation effects, space charge effects, structural changes and trapping effects are considered secondary.
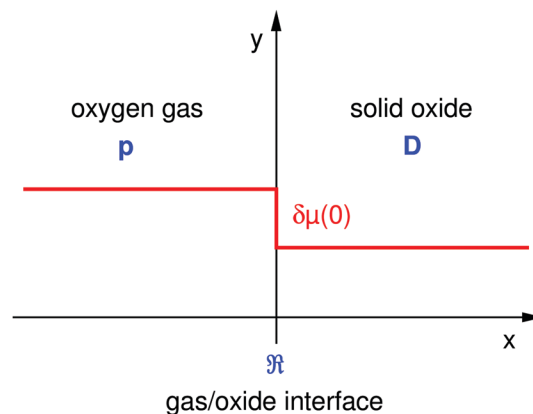

Fig. 1 Schematic representation of a gas/oxide interface of a homogeneous semi-infinite solid oxide. D is the self-diffusion coefficient of oxygen ions (D_O) in the solid oxide, p is the oxygen partial gas pressure (p_{O_2}) in the oxygen gas phase and $\Re$ is the equilibrium oxygen exchange rate ($\Re_O^0$) at the interface. At $t = 0$ a small step-like change $\delta\mu(0)$ of the chemical potential of oxygen ($\delta\mu_O(x = 0)$) is experimentally induced at the gas/oxide interface at $x = 0$.

Likewise the mathematical treatment is simplified by considering a homogeneous semi-infinite solid oxide (s. Fig. 1). In this case one has to consider only one gas/oxide interface at $x = 0$ where defect chemical reactions at the interface are quantified by the equilibrium oxygen exchange rate $\Re_O^0$. The diffusion process of oxygen ions in the solid oxide is quantified by the oxygen self-diffusion coefficient D_O. The oxygen partial pressure in the gas phase is given by p_{O_2}. That is, the considered oxide is phenomenologically described by two independent material parameters

$$\Re_O^0 = \Re_O^0(T, p_{O_2}), \quad D_O = D_O(T, p_{O_2}) \qquad (4)$$

which are functions of the temperature T and the oxygen partial pressure p_{O_2}, which control (together with unintentionally introduced impurities and/or deliberately added dopants) the concentration of oxygen vacancies $[V_O^{\bullet\bullet}]$ or interstitials $[O_i'']$ (and of the other ionic and electronic defects). The oxygen surface exchange coefficient K_O, however, is a phenomenological parameter which, a priori, is not yet related to a specific microscopic process *via* eqn (1). In view of the experimental findings outlined above it can be tentatively suggested that, at least for IEDP/SIMS and ECR experiments, but most probably also for PIE[9–11] and GPE/GPA[4,14,16] experiments, K_O should depend on the two independent parameters D_O and $\Re_O^0$ as follows

$$K_O = K_O(D_O, \Re_O^0) \qquad (5)$$

In order to derive the hypothetical function (5) from fundamental principal relations it is appropriate to adopt Maier's[6] notation and his very general procedure: the oxygen flux $j_O^K(0)$ through the surface (at $x = 0$) which is induced by a small change of the chemical potential of oxygen $\delta\mu_O(0)$ becomes[6]

$$j_O^K(0) = -\Lambda_O \delta\mu_O(0) = -\Lambda_O \frac{\partial\mu_O}{\partial c_O}\bigg|_{x=0} \delta c_O(0) = -K_O \delta c_O(0) \quad (6)$$

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where Λ_O is the conductance and $\partial\mu_O/\partial c_O$ the reciprocal "chemical" capacity. It is important to keep in mind that eqn (6) is an approximation near chemical equilibrium. It is very instructive to recall Maier's comment on eqn (6): "It is worth noting that these relationships [eqn (6)] are quite general in that they do not preselect a certain mechanism."[6] This statement implicitly comprises the fact that the parameter K_O principally can be the result of a combination of several mechanisms.

The diffusive oxygen flux[19] $j_O^D(0)$ in the near-surface region of thickness $\delta x(0)$, which is driven by the gradient of the chemical potential of oxygen $\partial\mu_O/\partial x|_{x=0}$, becomes

$$j_O^D(0) \cdot \delta x(0) = -\frac{D_O c_O(0)}{RT}\frac{\partial\mu_O}{\partial x}\bigg|_{x=0}\delta x(0) = -\frac{D_O c_O(0)}{RT}\delta\mu_O(0) \tag{7}$$

where D_O is the oxygen self-diffusion coefficient and $c_O(0)$ is the oxygen concentration (at the surface).

The first step in the derivation of the hypothetical function (5) is to study the correlation between K_O and D_O which principally results from the boundary condition at the gas/solid interface

$$j_O^D(0) = j_O^K(0) \tag{8}$$

which connects surface exchange and bulk transport and which therefore has to be respected when solving the respective diffusion equation.[20] With eqn (6) and (7) the boundary condition eqn (8) yields

$$\left(-\Lambda_O\delta x(0) + \frac{D_O c_O(0)}{RT}\right)\delta\mu_O(0) = 0 \tag{9}$$

This means that for a moderate value of $\delta\mu_O(0)$, i.e. a near-equilibrium situation at the surface, the (standard) boundary condition eqn (8) yields the relation $D_O c_O(0)/RT = \Lambda_O\delta x(0)$. With the thermodynamic factor $w_O(0)$ (s. eqn (2)) and $K_O = \Lambda_O\partial\mu_O/\partial c_O|_{x=0}$ (s. eqn (6)) one finally obtains the following general correlation between K_O and D_O which is valid in the near-equilibrium situation

$$\delta x(0)\cdot K_O = w_O(0)\cdot D_O \tag{10}$$

In the second step the meaning of the parameter $\delta x(0)$ will be clarified. For an isotope exchange experiment $w_O(0) = 1$ is valid and eqn (10) simply becomes $\delta x^\star(0) = D_O^\star/K_O^\star$, which is equivalent to the so-called characteristic length l_c^0 used in the literature to roughly estimate in which kinetic regime a given oxygen exchange experiment is performed. Adopting this notation the subsequent discussion will be facilitated for the reader as eqn (10) now becomes

$$\frac{l_c^0}{w_O(0)} = \frac{D_O}{K_O} \tag{11}$$

Here the upper case index 0 means that l_c^0 refers to a near-surface layer (at $x = 0$). Until now eqn (11) was only a formal mathematical rule to calculate l_c^0 and results as such directly from the boundary condition eqn (8). The physical meaning of l_c^0 will become evident if one defines with eqn (11) a

characteristic time t_c^0 (valid likewise for the near-surface region at $x = 0$) as follows

$$t_c^0 \equiv \frac{l_c^0}{w_O(0)K_O} = \frac{D_O}{K_O^2} \tag{12}$$

In Appendix A it is demonstrated that the characteristic time t_c^0 physically corresponds to the relaxation time of a (sufficiently small) change in the oxygen potential $\delta\mu(0)$ at the surface. Eqn (12) leads to the following two relations

$$l_c^0 = w_O(0)\sqrt{D_O t_c^0}; \quad K_O = \sqrt{\frac{D_O}{t_c^0}} \tag{13}$$

The characteristic length l_c^0 is thus proportional to the diffusion length the oxygen ions cover in the near-surface region during the characteristic time t_c^0. The term $K_O/\Delta x$ (as formulated by Maier[6]) in eqn (2) can be considered equivalent to the inverse characteristic time t_c^0. This relation suggests to postulate

$$t_c^0 \overset{!}{=} \frac{c_O(0)}{w(0)\cdot\mathfrak{R}_O^0} \tag{14}$$

Combining eqn (13) and (14) yields the missing correlation anticipated as "the hypothetical function" in eqn (5)

$$K_O^{h\to\infty} = \left(w_O(0)\cdot D_O\cdot\frac{\mathfrak{R}_O^0}{c_O(0)}\right)^{1/2} \tag{15}$$

It should be recalled that eqn (15) is a consequence of a boundary condition, and hence, is valid in all experimental situations where the considered boundary condition (eqn (8)) is valid. The upper case index $h\to\infty$ refers to the fact that this boundary condition is often applicable to plate-like samples of large thickness h, that is, if $h \gg l_c^0$.

For an oxygen isotope exchange experiment (with $w_O(0) = 1$ and $D_O^\star = f_O\cdot D_O$) eqn (15) becomes (dropping the index $h\to\infty$ in order to simplify the notation in eqn (16)–(19))

$$(K_O^\star)^2 = D_O^\star\cdot\frac{\mathfrak{R}_O^0}{c_O(0)} = f_O\cdot D_O\cdot\frac{\mathfrak{R}_O^0}{c_O(0)} \tag{16}$$

Here $(K_O^\star, D_O^\star)$ are data couples determined via an isotope exchange experiment. In a chemical oxygen exchange experiment (with $w(0) \gg 1$[21,22] and $\tilde{D}_O = w_O(0)\cdot D_O$) the data couples $(\tilde{K}_O, \tilde{D}_O)$ are determined. In this case eqn (15) yields

$$(\tilde{K}_O)^2 = \tilde{D}_O\frac{\mathfrak{R}_O^0}{c_O(0)} = w_O(0)\cdot\frac{D_O^\star}{f_O}\cdot\frac{\mathfrak{R}_O^0}{c_O(0)} = \frac{w_O(0)}{f_O}(K_O^\star)^2 \tag{17}$$

that is, one has $\tilde{K}_O = (w_O(0)/f_O)^{1/2}\cdot K_O^\star$ in contrast to $\tilde{D}_O = (w_O(0)/f_O)\cdot D_O^\star$. Comparing K_O/D_O ratios for the isotope exchange and for the chemical exchange experiment, respectively, one obtains from eqn (16) and (17) the following theoretical relations

$$\frac{K_O^\star}{D_O^\star} = \sqrt{\frac{w_O(0)}{f_O}}\frac{\tilde{K}_O}{\tilde{D}_O} = \left(\frac{\mathfrak{R}_O^0}{f_O\cdot D_O c_O(0)}\right)^{1/2} \tag{18}$$

Because of $f_O \approx 1$ and $w_O(0) \gg 1$[21,22] one immediately obtains $K_O^\star/D_O^\star > \tilde{K}_O/\tilde{D}_O$, which is in agreement with a large number of experimental results.[7] Thus eqn (18) supports the postulate expressed in eqn (14).

For more complicated sample geometries and correspondingly more complicated boundary conditions a more complicated correlation than eqn (15) is to be expected. The formal calculation of a characteristic length l_c^0 by eqn (11) is mathematically always possible, but the result would mask the physical meaning of l_c^0 which is explicitly expressed in eqn (13) only. Likewise the characteristic time t_c^0 has been (almost completely) neglected in the materials science literature, which focuses practically exclusively on K_O. It is, however, principally preferable for the discussion of experimental studies to consider the two characteristic parameters t_c^0 and l_c^0 compiled together with K_O in eqn (19)

$$t_c^0 = \frac{c_O(0)}{w(0) \cdot \mathfrak{R}_O^0}; \quad l_c^0 = w(0)\sqrt{D_O t_c^0}; \quad K_O = \sqrt{\frac{D_O}{t_c^0}}$$

$$\text{if} \quad h \gg l_c^0 \tag{19}$$

where h is the thickness of a plate-like sample. The set of eqn (19) shows that the condition $h \gg l_c^0$ is realised if the oxygen self-diffusion D_O is low and/or $\mathfrak{R}_O^0$ is high and/or $w(0)$ is small. This means that oxygen exchange occurs practically only in a near-surface region of characteristic thickness l_c^0 during the characteristic time t_c^0. Consequently the oxygen exchange of the *whole* sample is hindered due to the slow oxygen self-diffusion in the bulk. This situation corresponds to the so-called diffusion controlled regime.

The very specific condition $h \approx l_c^0$ means that within the characteristic time t_c^0 practically all the oxygen of the sample is exchanged. This scenario is called mixed regime as the oxygen exchange rate at the surface ($\mathfrak{R}_O^0$) and the self-diffusion coefficient in the bulk (D_O) hinder the overall oxygen exchange simultaneously. Note that the condition $h \approx l_c^0$ is more easily reached during chemical exchange (with $w(0) \gg 1$) than during isotope exchange (with $w(0) = 1$) because during chemical exchange oxygen self-diffusion is enhanced by the thermodynamic factor, $\tilde{D}_O = w_O(0)D_O$.

The condition $h \ll l_c^0$ means for a given value of h that the oxygen exchange at the sample surface is sufficiently slow and/or oxygen bulk transport is sufficiently rapid. In this case the oxygen exchange of the whole sample is entirely dominated by the (apparent equilibrium) oxygen exchange rate $\mathfrak{R}_O^0$ at the surface, and this corresponds to the so-called surface exchange regime. For a thin plate-like sample with thickness h and a sphere with radius r the solution of the diffusion equation for the oxygen exchange kinetics in the *surface exchange regime* can be approximated by

$$\frac{c_O(t) - c_O(0)}{c_O(\infty) - c_O(0)} = 1 - \exp\left(-\frac{t}{\tau_{eq}}\right) \tag{20}$$

where τ_{eq} is the time constant to reach chemical equilibrium.[17] For a plane sheet one gets $\tau_{eq} = (h/2)/K_O$ and for a sphere $\tau_{eq} = (r/3)/K_O$.[17] Recalling that K_O is a consequence of the boundary condition one concludes

Plane sheet: $\tau_{eq} \equiv t_c^0 = \dfrac{c_O(0)}{w(0)\mathfrak{R}_O^0}$; $\quad K_O^{h\to0} = \dfrac{h}{2}\dfrac{1}{t_c^0} = \dfrac{h}{2}w(0)\dfrac{\mathfrak{R}_O^0}{c_O(0)}$

Sphere: $\tau_{eq} \equiv t_c^0 = \dfrac{c_O(0)}{w(0)\mathfrak{R}_O^0}$; $\quad K_O^{r\to0} = \dfrac{r}{3}\dfrac{1}{t_c^0} = \dfrac{r}{3}w(0)\dfrac{\mathfrak{R}_O^0}{c_O(0)}$

$$\tag{21}$$

Comparing $K_O^{h\to\infty}$ for a thick plane sheet in eqn (15) with $K_O^{h,r\to0}$ for an extremely thin plane sheet or for powder samples, respectively, shows that, in the latter case, the oxygen exchange coefficient becomes independent of D_O. This means that the oxygen exchange rate $\mathfrak{R}_O^0$ can be directly determined from the time constant τ_{eq} in eqn (20), *e.g.* in an isothermal isotope exchange (IIE) experiment[13] or in a thermogravimetric relaxation experiment[17] carried out in the surface exchange regime. Further, eqn (21) suggests a direct experimental check of the postulate in eqn (14): if the postulate is valid the time constant τ_{eq} should not depend on the surface-to-volume ratio of the sample in the surface exchange regime.

The arguments displayed above offer a clue to explain the differences in the reported range of apparent activation energies (s. Armstrong *et al.*,[13] Table 5). Armstrong *et al.*[13] determined K_O values *via* IIE clearly in the surface exchange regime (spheres: 200–300 nm, $w_O(0) = 1$) according to eqn (21)

$$\text{Surface exchange regime:} \quad K_O^{r\to0} = \frac{r}{3}\frac{\mathfrak{R}_O^0}{c_O(0)} \tag{22}$$

Other studies (s. references compiled in Table 5 of Armstrong *et al.*[13]) which determined K_O values *via* IEDP/SIMS or ECR, respectively, as well as PIE-based[9–11] and GPE/GPA-based[4,14,16] investigations often remained in the diffusion controlled regime ($h \gg l_c^0$) and therefore unintentionally tended to determine a parameter corresponding to the following expression for the surface exchange coefficient

$$\text{Diffusion controlled regime:}$$

$$K_O^{h\to\infty} = \left(w_O(0) \cdot D_O \cdot \frac{\mathfrak{R}_O^0}{c_O(0)}\right)^{1/2} \tag{23}$$

The totally different temperature dependencies which are expected (activation energy for $\mathfrak{R}_O^0$ only in eqn (22) and the mean value of the activation energy for $\mathfrak{R}_O^0$ *and* for D_O in eqn (23)) comprise the reported range of apparent activation energies for the two entirely different experimental scenarios and further supports the postulate in eqn (14). Eqn (23) obviously allows to rationalise the $K_O \propto D_O^{1/2}$ correlation reported in the literature.[1]

In the following section it is demonstrated how the oxygen exchange rate $\mathfrak{R}_O^0$ can also be measured *via* an ^{18}O exchange experiment on a thick plate-like sample with SIMS depth profiling, that is, in an experimental situation where the oxygen exchange is clearly in the diffusion controlled regime, $h \gg l_c^0$. In 2001 Fielitz and Borchardt,[23] without, however, discussing the physical meaning of $\tau_{eq}{}^*$, pointed out that the corresponding solution of the diffusion equation as given by Crank[20] should be used in the following form

$$\frac{c(x,t) - c_\infty}{c_g - c_\infty}$$

$$= \text{erfc}\left(\frac{x}{\sigma^*}\right) - \exp\left(2\frac{x}{\sigma^*}\sqrt{\frac{t}{\tau_{eq}{}^*}} + \frac{t}{\tau_{eq}{}^*}\right)\text{erfc}\left(\frac{x}{\sigma^*} + \sqrt{\frac{t}{\tau_{eq}{}^*}}\right)$$

$$\text{with} \quad \sigma^* \equiv 2\sqrt{D_O{}^*t} \quad \text{and} \quad \tau_{eq}{}^* \equiv \frac{D_O{}^*}{(K_O{}^*)^2}$$

$$\tag{24}$$

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to fit SIMS depth profiles (s. elsewhere[23] for further details) in order to extract the tracer isotope diffusion length σ^* and the time constant τ_{eq}^* which is *the time necessary to obtain isotope equilibrium at the surface* ($x = 0$). As the boundary condition eqn (8) was used to solve the diffusion equation[20] one can use the set of eqn (19) (with $w_O(0) = 1$ for an isotope exchange experiment)

$$t_c^{0*} = \tau_{eq}^* = \frac{c_O(0)}{\Re_O^0}; \quad l_c^{0*} = \sqrt{D_O^* \cdot \tau_{eq}^*};$$

$$K_O^* = \sqrt{\frac{D_O^*}{\tau_{eq}^*}} = \sqrt{D_O^* \frac{\Re_O^0}{c_O(0)}} \tag{25}$$

This means that the oxygen exchange rate $\Re_O^0$ can be directly determined by the time constant τ_{eq}^* in eqn (24). It should be underlined that the specific form of the solution Fielitz and Borchardt[23] proposed explicitly contains the function $K_O^* = \sqrt{D_O^*/\tau_{eq}^*}$ (compare to τ_{eq}^* in eqn (24)), whereas this fact is not evident in the original form given by Crank.[20]

The presented revision of the principal nature of the surface exchange coefficient has been essentially triggered by the publications of Armstrong *et al.*[12,13] since these investigations demonstrated clearly that the experimentally determined apparent activation energies for K_O^* strongly depend on the kinetic regime of the respective experiments. Armstrong *et al.*[12,13] studied a relatively broad spectrum of materials (various perovskite MIECs like LC, LF, LSM, LSF, LSC or LSCF as well as two widely used oxygen electrolyte materials, namely YSZ and GDC). The similarities of the regime dependency of K_O^* therefore suggests that their observation does not reflect a specific property of a class of materials, but rather an underlying universal phenomenon. It should, however, be recalled that there is another method to determine K_O^* on powders which does not find any dependence of the apparent activation energies on the kinetic regime. Bouwmeester *et al.*[9] and Yoo *et al.*[10,11] used a novel pulse ^{18}O–^{16}O isotopic exchange (PIE) technique for the rapid determination of the oxygen surface exchange rate of oxide ion conductors. For this method powders with an average particle size in the range 0.4–5.0 μm are used. The reported apparent activation energies did not significantly differ from the values determined on bulk samples *via* IEDP/SIMS (or ECR, respectively). Recent GPE/GPA-based work[4,14,16] comprises similar activation energies for the surface exchange coefficient and for the oxygen diffusivity.

During the PIE experiment, a powder sample is loaded in a packed-bed micro-reactor. Maintaining conditions of chemical equilibrium, the response to an ^{18}O-enriched pulse fed through the reactor under continuous flow conditions is measured by mass spectrometric analysis of the gas phase fractions of oxygen isotopomers ($^{18}O_2$, $^{16}O^{18}O$ and $^{16}O_2$) at the exit of the reactor. The essential difference between PIE[9–11] and IIE[12,13] is the residence time between the $^{18}O_2$ atmosphere and the powder sample: for PIE the mean residence time is 5 to 40 ms,[9–11] whereas in an IIE experiment the residence time is 15 to 40 min.[12,13] In this context, it is worth recalling that the surface exchange

Table 1 Characteristic dimensionless parameters of the kinetic regimes

Kinetic regime	$L = (h/2)(K_O/D_O)$	$\phi(\beta_1, L)$	β_1^2
Surface control	<0.3	1	L
Mixed regime	0.3 to 30	—	—
Diffusion regime	>30	$8/\pi^2$	$\pi^2/4$

regime is not reached before the ^{18}O concentration gradient (in the bulk of a powder particle) practically disappears, which means that the value of D_O^* has become no longer relevant for the ^{18}O exchange process. Since principally a certain (finite) diffusion time t has to elapse before an ^{18}O concentration gradient in a particle with nominal radius r disappears, IIE seems to be more suitable than PIE to operate in a true surface exchange regime. This can be easily demonstrated by a straightforward estimation: the condition $\sqrt{D_O^* t} > r$ relates the necessary diffusion length, which is required to reach the surface exchange regime, to the particle radius. Estimating an average particle radius $r_{PIE} \approx 3$ μm[9–11] for the PIE experiment and an average particle radius $r_{IIE} \approx 0.3$ μm[12,13] for the IIE experiment one has $t_{PIE}/t_{IIE} = (r_{PIE}/r_{IIE})^2 \approx 100$ as a condition to reach the surface exchange regime in the published PIE studies compared to the published IIE studies. Since, however, the experimentally realized residence times t_{PIE} during the PIE experiment are only in the millisecond range,[9–11] so that one can estimate the ratio $t_{PIE}/t_{IIE} \approx 40$ ms/40 min = 1.7 × 10^{-5}, it cannot be excluded that PIE operates in a transitory, *i.e.* mixed controlled regime, similarly to the great majority of the published IEDP/SIMS studies.

Likewise the GPE/GPA-based investigations[4,14,16] use macroscopic samples and fairly long annealing times (for details see Appendix B). This inevitably implies a shift to L values typical for a mixed controlled or diffusion controlled regime (see Table 1 and Appendix C).

Summary

In 1998 Maier[6] proposed eqn (2) according to which the exchange rate $\Re_O^0$ (for oxygen) is proportional to the surface exchange coefficient K_O. Since then two well documented significant experimental findings became known which contradicted the general validity of eqn (2):

(i) Instead of the theoretically expected relation[15] $K_O^*/D_O^* \cong \tilde{K}_O/\tilde{D}_O$ the experiments yield[7] $K_O^*/D_O^* > \tilde{K}_O/\tilde{D}_O$.

(ii) If measured in the surface exchange regime ($h \ll l_c^0$) the apparent activation energies for K_O^* and $\tilde{K}_O$ are very small[13,17] whereas the apparent activation energies measured in the mixed controlled regime ($h \approx l_c^0$) or in the diffusion controlled regime ($h \gg l_c^0$) are considerably larger (s. Armstrong *et al.*,[13] Table 5).

These two surprising experimental observations, but especially the latter one, raise doubtful questions about the general validity of eqn (2), which necessitate a thorough fundamental rediscussion of the surface exchange coefficient for oxygen (on oxide surfaces).

Following principally Maier's[6] procedure the simplest possible experimental situation was chosen, *i.e.* an oxide surface close to chemical equilibrium (s. eqn (6)). For a complete picture, one has, however, to include the diffusive transport of oxygen (s. eqn (7)) and the fact that at the gas/solid interface there is a boundary condition to be respected. For the gas/solid interface of a homogeneous semi-infinite oxide this is eqn (8). This boundary condition inevitably leads to a mathematical correlation between K_O and D_O (s. eqn (11)), which, at first glance, seems to be only a formal recipe to calculate the so-called characteristic length l_c^0. Through the definition of a characteristic time t_c^0, this parameter can be attributed a physical meaning in eqn (13) as t_c^0 is the time necessary for the relaxation of a small change of the chemical potential of oxygen at the surface, $\delta\mu_O(0)$. Further, it becomes obvious that in eqn (2) the term $K_O/\Delta x$ (as formulated by Maier[6]) is equivalent to the inverse characteristic time t_c^0. It is therefore consistent to correlate the oxygen exchange rate $\mathfrak{R}_O^0$ and the characteristic time t_c^0 directly, as postulated through eqn (14). This postulate and the boundary condition (eqn (8)) entail an explicit dependency between the (surface) exchange rate and the (bulk) diffusivity of oxygen $K_O = K_O(D_O, \mathfrak{R}_O^0)$ (s. eqn (15)). At the same time such a dependency implies that for more complicated diffusion boundary conditions more complicated functions for K_O have to be expected.

The relations for K_O in the different kinetic regimes derived in the framework of the proposed novel interpretation of the standard theoretical concept[6] for K_O finally enable to unambiguously explain the two experimental observations (i) and (ii). In the presented model eqn (2) is only valid for the special case of the true surface exchange regime (s. eqn (21)). The parameter Δx in eqn (2), however, then is no longer a constant, but corresponds to the surface-to-volume ratio of the sample. As a consequence, the time constant τ_{eq} to reach equilibrium (s. eqn (20) and (21)) should not depend on the surface-to-volume ratio of the sample in the surface exchange regime.

Appendix A

For a thin surface layer $\delta x'(x = 0)$ the following expression can be formulated

$$\delta x'(0) = \frac{\delta x(0)}{w_O(0)} = \frac{l_c^0}{w_O(0)} \tag{A1}$$

If $\delta x'(0)$ is sufficiently small and/or if the oxygen flux $j_O^K(0)$ is approximately constant within the layer of thickness $\delta x'(0)$ one obtains with eqn (6)

$$\frac{d}{dt}c_O(0) = \frac{j_O^K(0)}{\delta x'(0)} = -\frac{\Lambda_O}{\delta x'(0)}\delta\mu_O(0) = \left.\frac{\partial c_O}{\partial \mu_O}\right|_{x=0}\frac{d}{dt}\delta\mu_O(0) \tag{A2}$$

That is, the time constant t_c^0 for the exponential relaxation kinetics of a small oxygen potential change $\delta\mu_O(0)$ at the surface is given by
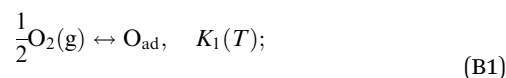
$$\frac{1}{t_c^0} = \frac{\Lambda_O}{\delta x'(0)}\left.\frac{\partial \mu_O}{\partial c_O}\right|_{x=0} \tag{A3}$$

Together with $K_O = \Lambda_O \partial\mu_O/\partial c_O|_{x=0}$ and eqn (A1), (A3) yields eqn (12).
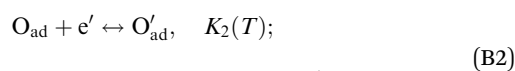
Appendix B

A widely applicable reaction model comprises the following consecutive steps:[7]
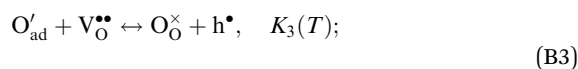
(1) adsorption dissociation (eq.)

$$\frac{1}{2}O_2(g) \leftrightarrow O_{ad}, \quad K_1(T);$$
$$\Re_1 = \vec{R}_1 - \overleftarrow{R}_1 = \vec{k}_1 p_{O_2}^{1/2} - \overleftarrow{k}_1[O_{ad}] \tag{B1}$$

(2) charge transfer (rds)

$$O_{ad} + e' \leftrightarrow O'_{ad}, \quad K_2(T);$$
$$\Re_2 = \vec{R}_2 - \overleftarrow{R}_2 = \vec{k}_2[O_{ad}][e'] - \overleftarrow{k}_2[O'_{ad}] \tag{B2}$$

(3) incorporation (eq.):

$$O'_{ad} + V_O^{\bullet\bullet} \leftrightarrow O_O^{\times} + h^{\bullet}, \quad K_3(T);$$
$$\Re_3 = \vec{R}_3 - \overleftarrow{R}_3 = \vec{k}_3[O'_{ad}][V_O^{\bullet\bullet}] - \overleftarrow{k}_3[O_O^{\times}][h^{\bullet}] \tag{B3}$$

The reactions are formulated according to the Kröger–Vink notation, using square brackets for the respective concentrations, K_n for the mass action constants (n = 1, 2, 3), $\vec{k}_n, \overleftarrow{k}_n$ for the forward/backward rate constants, $\vec{R}_n, \overleftarrow{R}_n$ for the forward/backward reaction rates and $\Re_n$ for the net reaction rates of these reactions. The so called apparent or effective equilibrium exchange rate $\mathfrak{R}_O^0$ of the rate determining step (charge transfer (B2) is often assumed as the rate determining step[7]) is defined by

$$\mathfrak{R}_O^0 = \sqrt{\overleftarrow{R}_2 \times \vec{R}_2} = \left(\overleftarrow{k}_2[O'_{ad}] \times \vec{k}_2[O_{ad}][e']\right)^{1/2} \tag{B4}$$

After inserting the mass action constants

$$K_1 = K_{ad} = \frac{\vec{k}_1}{\overleftarrow{k}_1} = \frac{[O_{ad}]}{p_{O_2}^{1/2}}; \quad K_3 = K_{inc} = \frac{\vec{k}_3}{\overleftarrow{k}_3} = \frac{[O_O^{\times}][h^{\bullet}]}{[O'_{ad}][V_O^{\bullet\bullet}]} \tag{B5}$$

into eqn (B4) and defining notational abbreviations $c_e \equiv [e'], c_h \equiv [h^{\bullet}], c_v \equiv [V_O^{\bullet\bullet}], c_O \equiv [O_O^{\times}]$ one finally gets if, *e.g.*, charge transfer is rate determining

$$\mathfrak{R}_O^0 = \left(\frac{\overleftarrow{k}_2\vec{k}_2 K_{ad}}{K_{inc}}\right)^{1/2}(c_O c_e c_h)^{1/2}\frac{p_{O_2}^{1/4}}{c_v^{1/2}} \tag{B6}$$

Eqn (B6) demonstrates in a very convincing manner that the surface exchange coefficient will have a non-trivial temperature dependence in the surface controlled regime ($K_O \propto \mathfrak{R}_O^0$, see eqn (21)). The resulting apparent activation energy should generally be less than the average energy of D_O and $\mathfrak{R}_O^0$. In the diffusion controlled regime ($K_O \propto \sqrt{D_O\mathfrak{R}_O^0}$, see eqn (15)) the resulting apparent activation energy is the average activation energy of D_O and $\mathfrak{R}_O^0$.

We will now demonstrate that there is an equivalence of the definitions of the phenomenological parameters used in

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Maier's approach[6] and the approach of Klier and Kučera.[24] Comparing both approaches it becomes evident that recent work,[4,14] based on the work of Klier and Kučera,[24] uses the same phenomenological description for their consecutive model as Maier[6] and the present authors (neglecting, however, the charge transfer step, which seems to be a weakness of this approach). With r_H for the "heterogeneous" reaction rate, r_a for the (dissociative) "adsorption" rate, and r_i for the "incorporation" rate they obtain (see eqn (8) and (12) in Farlenkov *et al.*[14]) $r_H = r_a \cdot r_i/(r_a + r_i)$, *i.e.* they set $1/r_H = 1/r_a + 1/r_i$ as expected for a consecutive model. In Maier's notation this would become $1/\Re^0 = 1/\Re_1 + 1/\Re_3$ if the charge transfer step (eqn (B2)) is neglected (in order to facilitate the comparison). In eqn (13) of Farlenkov *et al.*[14] the surface exchange coefficient, k, without specifying the kinetic regime, is defined as $k = $ const. $\times\, r_H$ (where the constant contains the specific data of the material, which have only a negligible temperature dependence). This corresponds formally to the relation originally proposed by Maier[6] as well as to our result for the mere surface controlled regime, $K_O = $ const. $\times \Re^0_O$, as expressed by eqn (21). It is, however, debatable (see Appendix C) whether the pure surface controlled regime can anyhow be studied if the dense (polycrystalline and single crystalline) samples have a thickness of 5 mm and undergo annealing times of more than 5×10^4 s.[14]

Appendix C

The most direct way to follow the kinetics of oxygen uptake or release *in situ* at high temperatures is a gravimetric experiment.[17] For plate-like samples with thickness h the mass change, $\Delta m(t)$, if normalized to the mass change at equilibrium, $\Delta m(t_{eq})$, is given by (Crank[20] p. 60)

$$\frac{\Delta m(t)}{\Delta m(t_{eq})} = 1 - \sum_{n=1}^{\infty} \frac{2L^2}{\beta_n^2(\beta_n^2 + L^2 + L)} \exp\left(-\beta_n^2 \frac{D_O t}{(h/2)^2}\right)$$

$$\text{with} \quad L \equiv \frac{h}{2}\frac{K_O}{D_O}$$

(C1)

The dimensionless quantities β_n are positive roots of $\beta_n \tan \beta_n = L$. As the infinite sum in eqn (C1) converges rapidly one has approximately[17]

$$\frac{\Delta m(t)}{\Delta m(t_{eq})} \approx 1 - \frac{2L^2}{\beta_1^2(\beta_1^2 + L^2 + L)} \exp\left(-\beta_1^2 \frac{D_O t}{(h/2)^2}\right)$$

$$= 1 - \phi(\beta_1, L) \exp\left(-\beta_1^2 \frac{D_O t}{(h/2)^2}\right)$$

(C2)

where D_O is the effective oxygen diffusion coefficient in the solid and K_O is the oxygen surface exchange coefficient defined by eqn (1). Positive roots of $\beta_1 \tan \beta_1 = L$ are plotted in Fig. 2 which allows a graphical visualisation of the kinetic regimes. The values of the resulting characteristic dimensionless parameters of the kinetic regimes are compiled in Table 1.
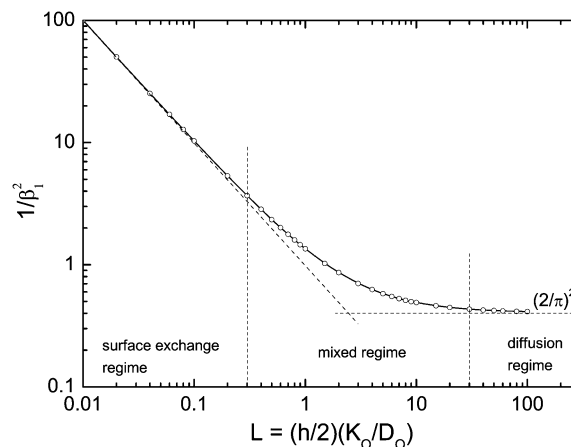

Fig. 2 Graphical visualisation of the kinetic regimes[17] (open points are positive roots of $\beta_1 \tan \beta_1 = L$ tabulated by Carslaw and Jaeger[25]). The diffusion regime is characterised by $\beta_1^2 \simeq \pi^2/4$ and the surface exchange regime by $\beta_1^2 \simeq L$.

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